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A STUDY OF THE NATURE OF THE CHEMICAL CHARACTERISTICS OF PARTICULATES COLLECTED FROM AMBIENT AIR

W. M. Henry, et al

Battelle Memorial Institute

Prepared for:

Department of Health, Education and Welfare

14 August 1970

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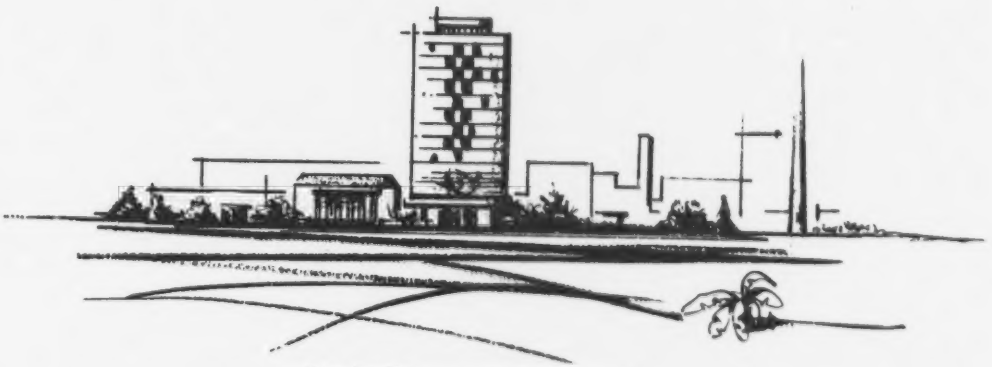

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The elemental composition of particulate material collected from the ambient urban air in six locations is presented. Both major and minor constituents were determined by utilizing several techniques and analytical instruments. In a broad sense the compositions for each city were similar; but certain distinct differences, especially in the less abundant elements, are apparent. Some work has been begun to identify compounds and elemental associations. This work is presently under way in a continuing program.

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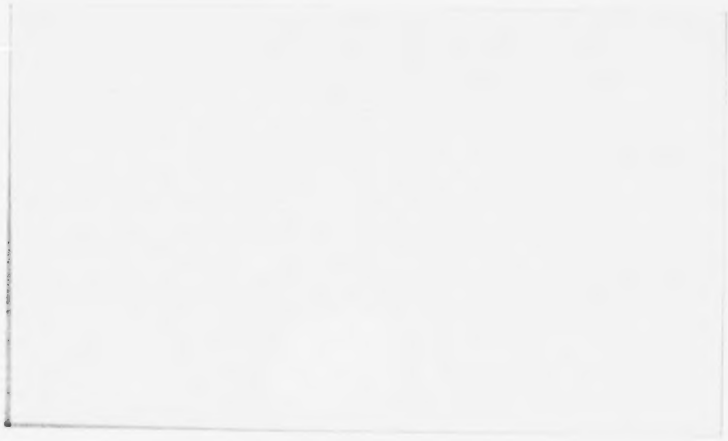

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APTD - 1519

A STUDY OF THE NATURE OF THE CHEMICAL CHARACTERISTICS OF PARTICULATES COLLECTED FROM AMBIENT AIR

FINAL REPORT

Covering the Period
June 30, 1969, to August 15, 1970

Contract CPA 22-69-153

Prepared for: Department of Health, Education, and Welfare
National Air Pollution Control Administration
Division of Air Quality and Emission Data

Principal Investigator: W. M. Henry
Author: E. R. Blosser

August 14, 1970

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August 14, 1970

Dr. Richard J. Thompson
Chief, Laboratory Services Branch
Division of Air Quality and Emission Data
National Air Pollution Control Administration
4676 Columbia Parkway
Cincinnati, Ohio 45226

Dear Dr. Thompson:

Ref. Contract CPA 22-69-153

This is the Final Report called for in the revised report schedule as specified in the supplemental agreement dated February 10, 1970.

As nearly as possible, the changes as suggested by you and Dr. Enrione have been incorporated in this final draft revision. The rough-draft copies were approved by you, subject to the revisions, by telephone July 27, 1970.

No further work is planned on this project. On a related contract, CPA 70-159, work is continuing on this research. Major emphasis is being placed on the identification of specific chemical species including compounds, minerals, ions, and molecules.

Very truly yours,

W M. Henry / ERD

William M. Henry, Chief
Materials Characterization
Research Division

WMH:cm

cc: Mr. John H. DeFord
Contracting Officer
NAPCA
Durham, North Carolina 27701

MANAGEMENT SUMMARY

Contract CPA 22-69-153

"A Study of the Nature of the Chemical Characteristics of Particulates Collected From Ambient Air".

Objective of Research

This program was designed to produce a complete elemental chemical analysis of the air particulates in selected urban environments.

Significance of Research Results to Date

With only a few exceptions, every element in the periodic chart has been sought in the particulates collected in six cities. These data, summarized in two tables in this report and in more detail in sixteen tables in the Appendix, are expected to be of interest to health physicists, pollution control administrators, and others involved with air quality. The data provide a base for future and current studies in related research topics.

Application of Research Results

The tabulated and pictorial data can be used directly, for example, to describe the levels of specific elements in urban air. They can also be used in studies directed toward describing the compounds and materials that comprise the particulates.

Goals for Next Period

No further work is scheduled under the present contract. A new contract, CPA 70-159, calls for the identification of species as mentioned above.

FOREWORD

The work described in this report was performed under the professional and administrative supervision of Mr. William M. Henry, with Mr. E. R. Blosser assisting. It is a pleasure to acknowledge the contributions of others of the Battelle staff, including D. L. Chase, R. L. Foltz, R. E. Heffelfinger, R. B. Iden, D. K. Landstrom, C. W. Melton, and D. C. Walters. Their efforts, and those of their assistants, made possible the compilation of data and figures included in this report.

A STUDY OF THE NATURE OF THE CHEMICAL CHARACTERISTICS OF PARTICULATES COLLECTED FROM AMBIENT AIR

by

E. R. Blosser

INTRODUCTION

The data collected on air particulate samples of ambient urban air pulled during the Winter and Spring of 1969-1970 in Cincinnati, St. Louis, Washington, D.C., Denver, Philadelphia, and Chicago are presented in this report. These data are the first comprehensive listings of specific elements to be found in the literature, and as such are a significant addition to the large body of knowledge that has been accumulated concerning the air in typical American cities.

Gaseous pollutants (NO_x, SO_2, CO, hydrocarbons) have been monitored for some time. Serious efforts in studying these compounds were begun in the 1940's, especially in problem areas such as Los Angeles. Elemental monitoring of key elements, lead being a prime example, began about the same time because it was becoming evident that many pollutants were caused by the leaded gasoline consumed by automobiles. More recently, the impact upon our environment by other sources – industries, individuals, utilities, agriculture – has received widespread publicity. For this reason, as a step in taking corrective action to reduce the particulate pollution of our air, the National Air Pollution Control Administration (NAPCA) decided to make a complete inventory of the elements present in urban air. Some of these undoubtedly arise from natural sources such as wind erosion of soil. Others originate from fuel combustion, and still others from industrial operations. In this report no attempt is made to pinpoint the specific sources of elements. Rather, the intent of this study is to provide base-line data upon which future studies of point sources, long-term trends, abatement effects, and other studies can be based.

EXPERIMENTAL WORK

Sample Collection and Preparation

Air particulate samples were collected on glass and cellulose ester filters* in six cities by NAPCA. The sampling stations are part of the Continuous Air Monitoring Program (CAMP) and employ "Hi-Vol" samplers. These use a series-wound motor ("vacuum sweeper") pulling air down through the filter which is supported on a wire grid. The units have roofs to protect the filter from gross falling contamination. Each filter represents 1 to 2 weeks of sampling, had from 0.8 to 4 grams of particulate deposited, and passed from 6,000 to 13,000 cubic meters of air. The details of the sampling dates, volumes, and weights are given in the Appendix.

Each filter was processed in several ways. The analytical samples were prepared by ashing (cellulose ester filters), by ultrasonically shaking the particulate from both glass and cellulose filters in benzene, by acid leaching, and by grinding the filter with the sample (glass filters). Each method has its advantages, but in general it is desirable to separate the sample from the filter matrix. When this is not done, as in the case when the glass filter is ground with the sample, blank contamination and matrix contributions become significant in some techniques. On the other hand, the less chemical or thermal treatment that is performed on a sample, the less the chance of losing certain elements such as mercury and selenium.

*Glass filters were supplied by Gelman, cellulose ester filters by Millipore.

Analytical Techniques

The specific analytical techniques that were employed, and the information they are best suited to provide are described below.

Spark-Source Mass Spectrography (SSMS)

This technique gives complete elemental coverage with (as used in this laboratory) semiquantitative accuracy. It is most useful for elements present at trace levels and for elements difficult to determine by other means.

Optical Emission Spectrography (OES)

Major to moderately low trace metals are determined by this technique. The data are at least semiquantitative, and spectral interferences from organic compounds (either particulate or from the filter itself) are nil.

Wet (Classical) Chemistry (Chem)

Specific elements are determined by various methods, including combustion, titration, atomic absorption, colorimetry, and distillation. These methods are generally accepted as relatively accura provided the possible interferences are known and allowed for.

X-Ray Fluorescence (XRF)

Once standardized, this technique provides accurate, rapid analyses of elements heavier than sodium. In the present work, ashed samples were used, but on a routine basis it should be possible to analyze the cellulose ester filters directly if corrections for the carbon absorption are made.

Optical (Light) Microscopy (OM)

Although difficult to quantify, this step is very useful in describing the morphology of particles larger than about 0.5 μ. Discrete entities such as soot, flyash, minerals, insect parts, etc., can be identified.

Electron Microscopy (EM)

Particles down to the angstrom range can be identified, and some small but important species such as asbestos fibers were found in several samples. As in the case of optical microscopy, quantification is difficult.

Electron Microprobe (EMP)

This technique is most useful when determining the distribution of elements in a sample, and when elemental associations in individual particles are desired. The basic gram detectability of this instrument is better than that of any other technique commercially available today.

Gas Mass Spectrometry (GMS)

The adsorbed gases on air particulates were analyzed using this technique. It is capable of good accuracy and extreme detectability for specific compounds. For particulate analysis, either thermal or chemical means must be employed to obtain a sample in the gas phase.

High-Resolution Mass Spectrometry (HRMS)

Because every combination of atoms has a slightly different mass because of elemental mass defects, HRMS can, in many cases, give the elemental formula for compounds. In the present work it was employed to search for organometallic compounds in the benzene-soluble phase of air particulates.

X-Ray Diffraction (XRD)

Crystalline materials can be identified by this technique. A computer program is used to compare the measured lines on the diffraction film with the library of known reference compounds. Some care must be taken in interpreting the data because X-ray lines of several compounds may overlap at any given measured distance.

RESULTS

The elemental data obtained are summarized in Table 1. The range found for each element in the six cities, together with a typical value, is presented. The latter is more or less a combination of an arithmetical average and a median value, with some subjective weighting, depending on the individual results. Specific data for each city, and other data generated in this work, are included in the Appendix. When evaluating these data from a health standpoint, one can assume that over a 70-year lifetime, a person will breathe about 3×10^5 cubic meters. Thus, if an element is present at the 3000-nanogram level, approximately 1 gram will be inhaled during a lifetime. Fortunately, much of the inhaled particulate is exhaled or is trapped before entering the lungs.

Elemental Analysis

As a first approximation, the air particulates in each of the six cities are similar. That is to say, carbon, silicon, calcium, aluminum, sodium, iron, sulfur, and lead predominate. Looking at the data in the Typical column in Table 1 (and at the data in Tables A-14 and A-16), it is seen that roughly one-half of the particulate matter is benzene soluble, or organic. The other half is mainly silica with major amounts of other materials including minerals and flyash. These facts were established by XRD, OM, and EM. See Table 2 for elemental analysis of the particulates collected in these cities. It should be noted that these are, in most cases, values obtained on more than 1 filter and by more than 1 method.

Beyond this broad observation, however, are significant differences. For example, of the six cities sampled, Chicago had the highest carbon and hydrogen content, and Washington and Cincinnati the least. Washington, Chicago, and Philadelphia, however, had the highest vanadium by nearly a factor of 10. Chlorine ranged from very low values in Philadelphia to high in Chicago and Denver. Lead is high and fairly uniform in all six cities, probably reflecting the density of automobile traffic in any urban area. The rare earths are not as rare as sometimes thought; about one-half of these elements were detected in all cities. Some very toxic elements – Se, Te, Tl, Hg – were either not detected or were found only at quite low levels. There is some uncertainty about mercury, because if it is present as the

element it would not be caught on filters but would pass through as a gas. Other elements may be present as gases, such as H_2S, H_2Se, etc. The use of silver filters to form an amalgam or compound might solve this problem.

Organometallic Compounds

Since the normal procedure for analyzing air particulate involves a preliminary benzene extraction to remove the organic phase, the presence of organometallic compounds would be overlooked in the insoluble phase. Even in this present work, when no extraction was made in most cases, ashing or even room-temperature evaporation might volatilize some organometallic compounds. Therefore, the benzene-soluble phase from one glass filter from each city was examined by HRMS. No identifiable organometallic compounds were found. If present, they should have been seen as peaks having negative mass defects, as compared with hydrocarbons which have positive mass defects. The benzene was also evaporated at room temperature and the residue remaining was examined by SSMS. Most of the elements present in significant amounts in the overall sample were also found in the extract residue, but in quantities (in terms of nanograms/M^3) very much lower than in the bulk sample. Two exceptions were noted: bromine and iodine. These two elements are extracted almost quantitatively.

Adsorbed Gases

Some SO_2, NO_x, H_2S, HCl, and CO_2 were found to be desorbed from the particulate matter on glass filters. The amount was small, and amounts to about a tenth-percent of the total sample weight. Some correlation was noted between the amount of carbon and the amount of desorbed gas, as might be expected if the carbon ("soot") could be considered a form of activated charcoal.

Optical and Electron Microscopy

The usual particles that have been identified previously were found in these samples. These include flyash, soot*, fibers, asbestos, and minerals. Color pictures of typical material from each city are included in the Appendix. Electron microscopy revealed many fine particles below optical visibility. Many were opaque amorphous particles (probably soot from combustion) that had not been reported previously. A few asbestos fibers were also found, emphasizing the importance of monitoring this pollutant. This pollutant is currently being studied in another program at Battelle-Columbus, and has been found to run as high as 1 $\mu g/m^3$ for point sources, and more nearly 1 nanogram for average ambient urban air.

Compound Identification

Work on this aspect of particulate analysis is just getting under way as the second year begins. However, a start was made during the last quarter of this present program. X-ray diffraction techniques were used to identify SiO_2 (α-quartz) and other classes of compounds. Electron microprobe studies were made to establish elemental associations in particles and areas.

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*Flyash and soot may be defined as "a particulate effluent from a combustion operation" (Walter C. McCrone, The Particle Atlas).

TABLE 1. RANGE AND TYPICAL VALUES FOR ELEMENTS IN PARTICULATES COLLECTED FROM AMBIENT URBAN AIR[a]

(Nanograms/cubic meter)

Element	Low	High	Typical
H total	3,000.	11,600.	5,000.
"Inorganic"[b]	1,600.	4,700.	3,000.
He	---------not sought----------		
Li	2.	20.	4.
Be	0.01	0.6	0.2
B	3.	30.	5.
C total	28,000.	110,000.	50,000.
"Inorganic"[b]	15,000.	50,100.	25,000.
N total	2,400.	9,700.	4,000.
"Inorganic"[b]	2,100.	7,800.	3,000.
O	-------not determined--------		
F	20.	900.	50.
Ne	---------not sought----------		
Na	500.	12,000.	2,000.
Mg	1,000.	5,000.	2,000.
Al	1,000.	10,000.	3,000.
Si	4,000.	45,000.	10,000.
P	50.	600.	100.
S total	3,000.	11,000.	5,000.
"Inorganic"[b]	1,700.	8,700.	4,000.
Cl	<4.	13,000.	1,000.
Ar	---------not sought----------		
K	600.	10,000.	1,000.
Ca	2,000.	20,000.	6,000.
Sc	1.	10.	1.
Ti	150.	600.	200.
V	1.	300.	30.
Cr	3.	50.	20.
Mn	30.	200.	100.
Fe	1,500.	9,000.	4,000.
Co	3.	10.	5.
Ni	2.	100.	20.
Cu	100.	3,000.	500.
Zn	200.	3,000.	500.
Ga	3.	8.	5.
Ge	<0.4	10.	2.
As	2.	100.	10.
Se	2.	20.	4.
Br	10.	200.	100.
Kr	----not sought-------		
Rb	10.	100.	20.
Sr	20.	200.	40.
Y	1.	5.	2.
Zr	2.	20.	4.
Nb	0.3	4.	0.5
Mo	0.5	10.	1.
Tc	----not sought-------		
Ru	<0.01	<0.1	<0.03
Rh	<0.01	<0.1	<0.03
Pd	<0.2	<1.	<0.3
Ag	0.5	20.	1.
Cd	<0.3	20.	1.
In	<0.5	<2.	<1.
Sn	6.	200.	50.
Sb	2.	60.	5.
Te	<0.1	0.2	<0.1
I	≤0.01	0.1	0.04
Xe	----not sought-------		
Cs	0.3	3.	1.
Ba	10.	500.	100.
La	2.	20.	5.
Ce	3.	20.	5.
Pr	1.	5.	2.
Nd	1.	10.	5.
Sm	0.4	2.	1.
Eu	0.1	0.5	0.2
Gd	0.3	1.	0.6
Tb	0.05	0.2	0.1
Dy	<0.2	1.	0.2
Ho	0.03	0.1	0.03
Er	<0.3	0.5	<0.3
Tm	<0.03	<0.1	<0.06
Yb	<0.05	0.3	<0.1
Lu	<0.02	0.3	<0.05
Hf	<0.04	<0.2	<0.05
Ta	<0.1	<0.3	<0.2
W	0.1	2.	1.
Re	<0.01	<0.06	<0.02
Os	<0.02	<0.06	<0.04
Ir	<0.01	<0.06	<0.02
Pt	<0.02	<0.1	<0.04
Au	<0.02	<0.1	<0.06
Hg	<0.02	<0.1	<0.04
Tl	≤0.01	0.1	<0.02
Pb	300.	5,000.	2,000.
Bi	0.2	2.	0.6
Po	-------not sought----------		
At	-------not sought----------		
Rn	-------not sought----------		
Fr	-------not sought----------		
Ra	-------not sought----------		
Ac	-------not sought----------		
Th	0.05	1.	0.2
Pa	------ -not sought----------		
U	0.05	2.	0.2
Transuranic elements not sought.			

(a) Chicago, Cincinnati, Denver, Philadelphia, St. Louis, Washington, D.C.

(b) Residue remaining after C_6H_6 extraction.

TABLE 2. APPROXIMATE ELEMENTAL CONCENTRATIONS FOUND IN PARTICULATES COLLECTED FROM AMBIENT URBAN AIR

(Nanograms/M^3)

Element	Cincinnati	Denver	St.Louis	Washington	Chicago	Philadelphia
H	3,000.	5,000.	7,000.	3,000.	10,000.	4,000.
Li	5.	20.	10.	3.	2.	2.
Be	0.2	0.04	0.4	0.1	<0.1	0.05
B	10.	20.	30.	10.	5.	5.
C	30,000.	40,000.	60,000.	30,000.	100,000.	30,000.
N	3,000.	2,000.	6,000.	2,000.	10,000.	5,000.
F	40.	400.	200.	100.	30.	20.
Na	4,000.	10,000.	10,000.	1,000.	5,000.	1,000.
Mg	1,000.	1,000.	2,000.	1,000.	5,000.	5,000.
Al	2,000.	7,000.	3,000.	2,000.	2,000.	3,000.
Si	5,000.	40,000.	6,000.	5,000.	6,000.	10,000.
P	100.	300.	200.	30.	60.	50.
S	4,000.	3,000.	8,000.	4,000.	3,000.	3,000.
Cl	1,000.	5,000.	1,000.	300.	10,000.	4.
K	1,000.	10,000.	2,000.	1,000.	2,000.	1,000.
Ca	6,000.	6,000.	20,000.	3,000.	10,000.	8,000.
Sc	<1.	2.	1.	1.	3.	10.
Ti	200.	400.	300.	200.	300.	400.
V	10.	20.	20.	100.	100.	200.
Cr	20.	20.	20.	10.	20.	40.
Mn	100.	100.	50.	50.	100.	200.
Fe	5,000.	5,000.	5,000.	2,000.	4,000.	4,000.
Co	5.	5.	3.	5.	10.	20.
Ni	20.	30.	20.	50.	40.	100.
Cu	300.	500.	3,000.	400.	400.	200.
Zn	1,000.	200.	3,000.	400.	500.	500.
Ga	5.	4.	10.	5.	6.	6.
Ge	5.	3.	5.	4.	7.	<0.4
As	20.	5.	50.	20.	60.	10.
Se	4.	2.	10.	5.	2.	2.
Br	50.	200.	300.	200.	100.	20.
Rb	10.	100.	20.	5.	20.	20.
Sr	10.	100.	50.	10.	40.	40.
Y	3.	4.	2.	1.	1.	2.
Zr	4.	20.	10.	4.	4.	10.
Nb	0.4	2.	1.	0.3	0.5	0.3
Mo	2.	5.	3.	2.	3.	2.
Ru	<0.04	<0.06	<0.04	<0.01	<1.	<0.03
Rh	<0.04	<0.2	<0.1	<0.03	<0.06	<0.01
Pd	≤0.2	<1.	<0.4	<0.1	<0.3	<0.3
Ag	<1.	1.	20.	0.6	2.	0.6
Cd	2.	1.	5.	0.3	3.	1.

TABLE 2. APPROXIMATE ELEMENTAL CONCENTRATIONS FOUND IN PARTICULATES COLLECTED FROM AMBIENT URBAN AIR (Continued)

Element	Cincinnati	Denver	St. Louis	Washington	Chicago	Philadelphia
In	<2.	<3.	<2.	<0.5	<1.	<1.
Sn	100.	10.	50.	20.	20.	40.
Sb	8.	5.	8.	3.	8.	60.
Te	≤0.2	<0.2	5.	0.3	≤0.2	≤0.1
I	0.5	2.	2.	4.	≤0.7	0.01
Cs	0.4	1.	1.	3.	0.7	0.4
Ba	50.	300.	100.	100.	50.	40.
La	2.	20.	2.	4.	5.	20.
Ce	3.	20.	3.	3.	7.	20.
Pr	1.	4.	1.	1.	2.	4.
Nd	3.	10.	3.	3.	5.	7.
Sm	0.4	1.	0.6	0.5	2.	1.
Eu	<0.2	0.5	<0.4	0.1	0.3	0.2
Gd	<0.6	1.	<1.	0.3	2.	0.6
Tb	<0.1	0.1	<0.2	0.05	≤0.1	0.2
Dy	<0.3	1.	<0.6	0.2	0.3	0.6
Ho	<0.1	0.1	<0.2	0.03	0.1	0.1
Er	<0.3	0.5	<0.6	<0.3	≤0.2	0.3
Tm	<0.06	<0.2	<0.1	<0.03	≤0.1	0.06
Yb	<0.2	<1.	<0.4	<0.3	≤0.5	0.3
Lu	<0.1	0.3	<0.2	<0.02	<0.1	≤0.04
Hf	<0.04	<0.6	<0.2	<0.05	<0.3	0.2
Ta	<0.1	<0.3	<0.3	≤0.05	≤0.1	≤0.2
W	0.2	2.	0.5	0.1	1.	1.
Re	<0.02	<0.05	<0.06	<0.01	<0.05	<0.02
Os	<0.02	<0.1	<0.06	<0.02	<0.04	<0.03
Ir	<0.02	<0.05	<0.03	<0.01	<0.02	<0.06
Pt	<0.03	<0.1	<0.1	<0.02	<0.04	<0.03
Au	<0.1	<0.1	<0.03	<0.02	<0.1	<0.06
Hg	<0.04	<0.1	<0.1	<0.05	<0.04	<0.03
Tl	<0.03	0.1	<0.1	≤0.02	≤0.01	0.04
Pb	1,000.	3,000.	3,000.	2,000.	4,000.	2,000.
Bi	0.5	1.	2.	0.3	2.	0.6
Th	0.1	0.6	1.	0.05	0.4	0.2
U	0.2	0.3	2.	0.05	0.2	0.2

SUMMARY

The data given in this report and the attached Appendix show the amounts of almost every natural element as found in ambient air particulates collected in six cities. Some significant differences were found in both major and trace elements. The morphology of the particulates is shown in optical and electron micrographs in the Appendix. Examples of the XRD and HRMS data output are also shown.

FUTURE WORK

No further work is planned under the present contract. A new contract has been negotiated, CPA 70-159. Under the new contract a detailed study of ions, molecules, and compounds is beginning. The new work, combined with the present report, should give a comprehensive view of the inorganic air particulates.

RATE OF EFFORT

Through June 30, 1970, the total expenses were $35,829.37 and $390 is committed for the nylon filters, leaving $9,980.63. About 1600 man-hours have been expended, exclusive of the effort to prepare this Final Report. It is expected that most of the remaining funds will be required for the preparation and reproduction of the Final Report.

APPENDIX

SUPPLEMENTARY DETAILS AND DATA

APPENDIX

SUPPLEMENTARY DETAILS AND DATA

Adsorbed Gases in Particulates

Procedure

An all-metal stainless steel sample container with appropriate valves, flanges, etc., was attached to the all-metal inlet of the ultrahigh-sensitivity AeroVac mass spectrometer. The entire system was baked, and the background established in the same manner as subsequently used for the sample analyses. This blank was essentially instrument background.

The procedure was designed to liberate at least some of the gases adsorbed on and absorbed in the particulate material (and probably on the filter itself). An extraction temperature of 130 C was chosen to minimize decomposition of the particulates. Almost no inorganic compounds likely to be in the air will be decomposed at that temperature, and past research has shown that natural products such as cereal grain are not decomposed significantly below about 150 C.

The designated sample size (area) was cut from the filter and was placed in the stainless steel container. The container was purged with helium purified by passing through a liquid-nitrogen-cooled trap. (The helium was analyzed without a sample or blank in the container and no significant impurities were detected.) After 15 minutes the container was isolated and cooled with a liquid-nitrogen-filled Dewar for 30 minutes. The helium was pumped from the system. This step also would remove H_2, CO, CH_4, and perhaps a few other low-boiling-point gases. The container was warmed to 130 C and held at that temperature for 30 minutes. The amount of gas released was measured and analyzed.

The sample left in the container was isolated and cooled to -80 C, using a Dry Ice-acetone bath, to obtain a spectrum without water and most of the hydrocarbon present. This method confirmed the presence of SO_2, NO_x, CO_2, and H_2S by showing that the hydrocarbon fragmentation patterns were not introducing a significant error at the mass-to-charge positions used to calculate the concentrations of the reported compounds.

The results are reported in Table A-1. They are reported as standard cc atmospheres rather than as grams per filter for two reasons. First, the samples have been exposed to various atmospheres since their collection in January. How much has been lost or picked up during that time is unknown. Second, it is not known, and it probably cannot be determined, how efficient the gas-evolution technique really is. In any case, the data are interesting on a comparative basis. For example, the results show somewhat less "harmful" gases in Denver than in the other areas. This correlates with two other observations. First, the spark-source mass-spectrographic spectra of the Denver samples (as physically removed from the Millipore filter, without extracting the organic phase) showed evidence of fewer organic compounds. Second, the sample, when examined by light and electron microscopy, had less soot and other carbon black particles than did the samples from the other three cities. These components can be considered as "activated charcoal" or at least as very active adsorbers.

The major compound removed from all the filters, including the blank, was water. It would account for at least 90 percent of the off gas. The breakdown of the individual nitrogen oxides is probably not very accurate, but it is surprising to see such a large proportion present as NO.

Values shown for m/e 43 do not include all the hydrocarbon present, but were included to indicate the comparative amount of these hydrocarbons having a major mass at m/e 43. No attempt was made to identify the hydrocarbons or to determine the total amount present.

TABLE A-1. EVOLVED GAS FROM PARTICULATE MATTER

Location	Washington	St. Louis	Cincinnati	Denver	Blank
Filter number	0006989	0006986	0006997	0006982	-
Sample size, cm^2	69	69	66	69	69
Net weight sample, g	0.12	0.29	0.14	0.59	-
Total evolved gas, cc-atm (STP)	5.10	9.55	8.49	14.8	0.86

Compound	cc Atmospheres Per Gram Particulate[(a)]				Total cc Atmospheres
SO_2	0.081	0.007	0.003	0.035	2×10^{-5}
CO_2	0.16	0.27	0.47	0.16	4×10^{-5}
NO_x	0.54	0.31	0.70	0.23	2×10^{-4}
NO	0.30	0.28	0.44	0.20	-
NO_2	0.04	0.02	0.10	0.01	-
N_2O	0.20	0.01	0.16	0.02	-
H_2S	0.009	0.007	0.016	0.003	1×10^{-4}
HCl	0.0005	0.0003	0.0008	0.0003	1×10^{-5}
m/e 43	0.032	0.062	0.036	0.019	1×10^{-4}

(a) Can be converted to grams by multiplying by the factor $\frac{\text{molecular weight}}{2.24 \times 10^4}$.
For example 0.54 cc atm NO_x in Washington is equivalent to about 0.08 percent of the total sample.

Note: Water and air components (O_2, N_2, and Ar) were not calculated.

Those values reported for hydrogen chloride should be considered the maximum values possible, since some hydrocarbon-fragment interference is possible and since they are approaching the blank level.

Elemental Analysis of Particulates

Procedure

Optical Emission Spectrographic. For both Millipore and glass filters the sample was removed from the filter by ultrasonic agitation in benzene. The filters were examined by optical microscopy after this treatment. Some particles remained on or in the glass filters, but essentially all were removed from the Millipore. The suspension was dried and then ashed at 500 C. Almost no elements detectable by this technique would be lost in this process. (Mercury would probably be volatilized, however; therefore, special analyses were made for that element.) The ignited residues were mixed with germanium and carbon in the ratio 1:9:10 (sample:Ge:C) and arced in graphite electrodes. Synthetic standards were run on each film as references.

The last group of filters (Chicago and Philadelphia) were examined by a slightly modified technique. The Millipore filter was ashed directly rather than performing the extraction step, avoiding any possibility of incomplete sample removal. The Millipore blank introduces no detectable error.

Mercury was determined directly on Millipore filters using a "boiler cap" technique. Samples were run from Cincinnati, St. Louis, Denver, and Washington. These "boiler cap" data are included in the OES results in Tables A-2 through A-5.

Spark-Source Mass Spectrographic. Three sample preparation techniques were employed. In each case the sample was briquetted with graphite.

(1) The sample was removed from Millipore and glass filters by ultrasonic agitation in benzene, then dried but not ashed. This is referred to as "C_6H_6 Wash" in the following tables.

(2) Millipore filters were ashed at 500 C. This is referred to as "Ash".

(3) The glass filters were ground in an agate (SiO_2) mortar.

In no case was a benzene extraction per se made. In other words, any trace metals in the organic (benzene soluble) phase would be detected. The organic compounds did cause some spectral interferences. On the other hand, in the ground-glass filter there is no possibility of loss of volatile components except those lost at room temperature in vacuum, such as metallic mercury.

The samples were briquetted isostatically with graphite in polyethylene dies. They were sparked for a series of exposures of varying intensities. The resulting photoplates were read visually. Elemental concentrations were estimated by noting in which exposure a given isotopic line was just detectable.

X-Ray Fluorescence. Samples were prepared by ashing the Millipore filters with the particulates. A fixed weight of sample ash was mixed with $Li_2B_4O_7{\cdot}5H_2O$ and briquetted in round aluminum dies. Synthetic standards were prepared to duplicate closely the range of impurities in the samples.

Wet Chemistry. Atomic absorption was employed to determine Na, K, Ca, Mg, Fe, Cu, Pb, and Zn. Millipore filters were ashed, and the residue was dissolved in acid. Appropriate aliquots were then analyzed and compared with synthetic standards.

Chlorine was determined by a colorimetric method on an acid leach from glass filters, and fluorine by a distillation technique from glass filters. Unfortunately the fluorine blank of the glass filters is quite high. Nitrogen, carbon, and hydrogen were determined using a CHN analyzer (based on the Dumas-Pregel method) to burn the glass filters. Sulfur was determined by a combustion technique using glass filters.

It is recognized that ashing may cause the loss of certain elements such as Pb, Hg, Cd, and Se. However, a comparison of the data for nonashed samples with ashed samples shows no loss of volatile elements within the expected accuracy of the procedures. The exceptions to that statement are the elements bromine and iodine, which do appear to be lost by ashing in several instances. In any case, the reduction of spectral interferences by ashing is a sufficient advantage over nonashed or acid-leached samples to outweigh the disadvantage of losses. Those elements possibly lost can be determined on nonashed samples.

Oxygen. This is the one area where complete failure must be reported. Had it been possible to collect samples on silver as originally planned, it is virtually certain that oxygen could have been determined by vacuum fusion. But both glass and Millipore obviously contain large amounts of oxygen and therefore could not be analyzed directly. All attempts to separate the sample from its filter failed. Ultrasonic agitation removed small amounts of the filter, either glass or Millipore. Dissolving the Millipore in acetone and filtering on silver failed because the silver plugged almost immediately. In the future, if oxygen must be determined, it is imperative that another sampling approach be found.

Tabulated Data

The city-by-city elemental analyses of Millipore filters are given in Tables A-2 through A-7, with cross check data shown where available. Similar data are given for glass filters in Tables A-8 through A-13. Owing to the large number of data in some of the tables it was necessary to reduce them for reproduction. Also, abbreviations were used to conserve space and these are as follows:

M^3	Cubic meter
Ash	Ash from Millipore plus particulate
C_6H_6 Wash	Dried (not ignited) residue from ultrasonic removal of particles in benzene
SSMS	Spark-source mass spectrography
OES	Optical emission spectrography
Chem	Wet (classical chemistry including atomic absorption, combustion, etc.)
XRF	X-ray fluorescence

The analyses for H, C, and N are given in a separate table (Table A-14) to save space in the other tables.

TABLE A-2. ANALYSIS OF AIR PARTICULATES ON MILLIPORE - CINNCINNATI

(Nanograms/M^3)

Element	Sample Designation: M 000 417 (Ash) SSMS	OES	Chem	XRF	M 000 417 (C_6H_6 Wash) SSMS	M 428 (Ash) SSMS	OES	Chem	XRF	M 428 (C_6H_6 Wash) SSMS	M 000 416 (Ash) SSMS	OES	Chem	XRF	M 000 416 (C_6H_6 Wash) SSMS	M 000 405 (Ash) SSMS	OES	Chem	XRF	M 000 405 (C_6H_6 Wash) SSMS
Be	0.4	0.3	--	--	0.1	0.2	0.4	--	--	0.1	0.5	0.3	--	--	0.5	0.3	0.2	--	--	0.6
F	80.	--	--	--	30.	30.	--	--	--	60.	30.	--	--	--	60.	50.	--	--	--	200.
P	100.	--	--	550	50.	50.	--	--	600.	50.	50.	--	--	475.	50.	50.	--	--	--	50.
S	4000.	--	--	6400.	600.	2000.	--	--	3300.	2000.	2000.	--	--	5800.	2000.	1000.	--	--	40.	1000.
Cl	2000.	--	--	<5.	2000.	300.	--	--	15.	300.	300.	--	--	10.	300.	300.	--	--	.200.	300.
Ga	8.	--	--	--	8.	3.	--	--	--	3.	5.	--	--	--	5.	3.	--	--	<4.	<10.
As	10.	--	--	--	10.	4.	--	--	--	7.	10.	--	--	--	30.	10.	--	--	--	20.
Se	4.	--	--	--	4.	2.	--	--	--	4.	3.	--	--	--	6.	2.	--	--	--	5.
Br	80.	--	--	--	80.	10.	--	--	--	100.	6.	--	--	--	30.	10.	--	--	--	60.
Te	≤0.2	--	--	--	≤0.3	≤0.1	--	--	--	<2.	≤0.1	--	--	--	<0.2	≤0.1	--	--	--	2.
I	0.04	--	--	--	0.5	≤0.01	--	--	--	≤1.	<0.01	--	--	--	1.	≤0.01	--	--	--	2.
Hg	<0.03	<0.05	--	--	≤0.4	<0.03	<0.4	--	--	<3.	<0.03	<0.7	--	--	<0.3	<0.04	<0.4	--	--	<10.
Tl	≤0.02	--	--	--	<0.2	≤0.03	--	--	--	<1.	<0.02	--	--	--	<0.2	≤0.02	--	--	--	≤2.
Pb	1000.	500.	3750.	800.	600.	1000.	1400.	3200.	2300.	1500.	200.	360.	2600.	2100.	300.	1000.	1000.	3120.	3000.	1500.
Bi	0.6	--	--	--	0.6	0.4	--	--	--	<4.	0.5	--	--	--	0.5	1.	--	--	--	3.

Element	Sample Designation: M 000 417 (Ash) SSMS	OES	Chem	XRF	Element	M 000 417 (Ash) SSMS	OES	XRF	Element	M 428 OES	Chem	XRF	M 000 416 OES	Chem	XRF	M 000 405 (Ash) OES	Chem	XRF
Li	4.	--	--	--	In	<2.	--	--	Na	500.	750.	--	980.	3770.	--	260.	780.	--
B	10.	5.	--	--	Sn	500.	100.	150.	Mg	1500.	1750.	--	1300.	1170.	--	1540.	1500.	--
Na	4000.	1500.	6400.	--	Sb	10.	--	--	Al	3300.	--	2500.	2000.	--	3000.	2700.	--	2,800.
Mg	2000.	1500.	1500.	--	Cs	0.3	--	--	Si	9200.	--	7500.	4300.	--	7200.	7600.	--	8,000.
Al	1000.	2500.	--	2500.	Ba	100.(a)	25.	--	K	1000.	950.	1400.	1300.	1040.	1500.	1540.	840.	1,300.
Si	4000.	5000.	--	7000.	La	4.	--	--	Ca	7000.	6450.	8100.	4220.	4420.	5500.	5100.	6000.	17,300.
K	8000.	1000.	950.	1500.	Ce	10.	--	--	Ti	200.	--	170.	200.	200.	--	180.	--	220.
Ca	8000.	5000.	6000.	7000.	Pr	1.	--	--	V	1.3	--	12.	4.	20.	--	0.5	--	20.
Sc	≤1.	--	--	--	Nd	4.	--	--	Cr	3.	--	--	20.	--	--	20.	--	--
Ti	300.	150.	--	250.	Sm	0.4	--	--	Mn	25.	--	--	130.	--	--	135.	--	--
V	15.	5.	--	20.	Eu	<0.2	--	--	Fe	2500.	7700.	9200.	1950.	4750.	6100.	1500.	3870.	4,500.
Cr	40.	20.	--	--	Gd	<0.6	--	--	Co	7.	--	--	7.	--	--	4.	--	--
Mn	400.	150.	--	--	Tb	<0.1	--	--	Ni	2.	--	--	15.	--	--	1.	--	--
Fe	4000.	2500.	5700.	7300.	Dy	<0.3	--	--	Cu	150.	250.	125.	200.	650.	600.	88.	308.	160.
Co	15.	5.	--	--	Ho	<0.1	--	--	Zn	1000.	2200.	1600.	200.	1000.	--	440.	1450.	1,250.
Ni	30.(a)	15.	--	--	Er	<0.3	--	--	Zr	1.	--	--	7.	--	--	10.	--	--
Cu	300.(a)	150.	450.	350.	Tm	<0.06	--	--	Mo	7.	--	--	2.	--	--	45.	--	--
Zn	400.	500.	1950.	1500.	Yb	<0.2	--	--	Ag	1.	--	--	0.7	--	--	0.5	--	--
Ge	6.	--	--	--	Lu	<0.1	--	--	Sn	7.	--	13.	20.	45.	--	25.	--	120.
Rb	15.	--	--	--	Hf	<0.04	--	--	Ba	7.	--	--	20.	--	--	25.	--	--
Sr	40.	--	--	--	Ta	<0.1	--	--										
Y	2.	--	--	--	W	0.2	--	--										
Zr	4.	5.	--	--	Re	<0.02	--	--										
Nb	0.4	--	--	--	Os	<0.02	--	--										
Mo	2.	2.	--	--	Ir	<0.02	--	--										
Ru	<0.04	--	--	--	Pt	<0.03	--	--										
Rh	<0.04	--	--	--	Au	<0.1	--	--										
Pd	≤0.2	--	--	--	Th	0.1	--	--										
Ag	1.	1.	--	--	U	0.2	--	--										
Cd	0.6	--	--	--														

(a) SSMS results on C_6H_6 Wash: Ni, 15; Cu, 150; Sn, 100; Ba, 40.

TABLE A-3. ANALYSIS OF AIR PARTICULATES ON MILLIPORE - DENVER

(Nanograms/M^3)

Element	Sample Designation: M 000 412 (Ash) SSMS	OES	Chem	XRF	M 000 412 (C_6H_6 Wash) SSMS	M 000 413 (Ash) SSMS	OES	Chem	XRF	M 000 413 (C_6H_6 Wash) SSMS
Be	0.1	0.04	--	--	0.1	0.01	0.06	--	--	0.01
F	600.	--	--	--	600.	300.	--	--	--	300.
P	200.	--	--	250.	400.	200.	--	--	210.	200.
S	2,000.	--	--	3,700.	3,000.	1,000.	--	--	3,300.	2,000.
Cl	10,000.	--	--	5,000.	3,000.	300.	--	--	30.	400.
Ga	5.	--	--	--	10.	5.	--	--	--	5.
As	5.	--	--	--	5.	5.	--	--	--	5.
Se	2.	--	--	--	3.	≤1.	--	--	--	≤1.
Br	200.	--	--	--	200.	100.	--	--	--	200.
Te	<0.2	--	--	--	<0.4	≤0.2	--	--	--	≤0.4
I	0.1	--	--	--	2.	<0.02	--	--	--	4.
Hg	<0.1	0.4	--	--	<0.3	<0.1	<0.6	--	--	<0.3
Tl	0.1	--	--	--	0.2	0.1	--	--	--	<0.4
Pb	1,000.	1,600.	6,240.	700.	2,000.	2,000.	1,800.	5,820.	4,700.	1,000.
Bi	1.	--	--	--	1.	0.5	--	--	--	0.5

Element	Sample Designation: M 000 412 (Ash) SSMS	OES	Chem	XRF	Element	M 000 412 (Ash) SSMS	OES	Chem	XRF	Element	M 000 413 (Ash) OES	Chem	XRF
Li	20.	--	--	--	In	<3.	--	--	--	Na	1,00.	4,020.	--
B	20.	30.	--	--	Sn	6.	20.	--	--	Mg	900.	1,560.	--
Na	7,000.	4,000.	12,500.	--	Sb	5.	--	--	--	Al	9,070	--	8,500.
Mg	2,000.	1,200.	1,400.	--	Cs	2.	--	--	--	Si	27,800.	--	33,500.
Al	5,000.	10,000.	--	7,000.	Ba	500.	240.	--	--	K	9,000.	1,860.	6,600.
Si	High	44,000.	--	44,000.	La	20.	--	--	--	Ca	9,000.	6,900.	7,200.
K	10,000.	10,000.	1,800.	9,500.	Ce	20.	--	--	--	Ti	360.	--	260.
Ca	10,000.	7,000.	5,200.	6,500.	Pr	5.	--	--	--	V	18.	--	25.
Sc	2.	--	--	--	Nd	10.	--	--	--	Cr	18.	--	--
Ti	500.	400.	--	170.	Sm	1.	--	--	--	Mn	120.	--	--
V	30.	20.	--	30.	Eu	0.5	--	--	--	Fe	5,400.	8,820.	8,500.
Cr	20.	24.	--	--	Gd	1.	--	--	--	Co	6.	--	--
Mn	100.	120.	--	--	Tb	0.1	--	--	--	Ni	18.	--	--
Fe	5,000.	4,400.	8,000.	8,400.	Dy	1.	--	--	--	Cu	600.	600.	480.
Co	10.	8.	--	--	Ho	0.1	--	--	--	Zn	180.	420.	300.
Ni	50.	20.	--	--	Er	0.5	--	--	--	Zr	35.	--	--
Cu	500.	400.	590.	400.	Tm	<0.2	--	--	--	Mo	60.	--	--
Zn	30.	240.	390.	210.	Yb	<1.	--	--	--	Ag	1.	--	--
Ge	<2.	--	--	--	Lu	0.3	--	--	--	Sn	30.	--	<6.
Rb	100.	--	--	--	Hf	<0.6	--	--	--	Ba	360.	--	--
Sr	200.	--	--	--	Ta	<0.3	--	--	--				
Y	5.	--	--	--	W	2.	--	--	--				
Zr	10.	24.	--	--	Re	<0.05	--	--	--				
Nb	1.	--	--	--	Os	<0.1	--	--	--				
Mo	2.	8.	--	--	Ir	<0.05	--	--	--				
Ru	<0.06	--	--	--	Pt	<0.1	--	--	--				
Rh	<0.2	--	--	--	Au	<0.1	--	--	--				
Pd	<1.	--	--	--	Th	0.6	--	--	--				
Ag	2.	0.4	--	--	U	0.3							
Cd	0.6	--	--	--									

TABLE A-4. ANALYSIS OF AIR PARTICULATES ON MILLIPORE - ST. LOUIS

(Nanograms/M^3)

Element	Sample Designation: M 000 408 (Ash) SSMS	OES	Chem.	XRF	M 000 408 (C_6H_6 Wash) SSMS	M 000 409 (Ash) SSMS	OES	Chem	XRF	M 000 409 (C_6H_6 Wash) SSMS
Be	0.6	0.3	--	--	0.4	0.6	0.3	--	--	0.3
F	200.	--	--	--	200.	300.	--	--	--	300.
P	200.	--	--	185.	200.	200.	--	--	125.	300.
S	5,000.	--	--	16,000.	5,000.	5,000.	--	--	11,000.	15,000.
Cl	1,500.	--	--	60.	1,500.	5,000.	--	--	7,200.	3,000.
Ga	5.	--	--	--	20.	3.	--	--	--	10.
As	100.	--	--	--	300.	20.	--	--	--	30.
Se	10.	--	--	--	30.	3.	--	--	--	6.
Br	100.	--	--	--	300.	700.	--	--	--	1,500.
Te	10.	--	--	--	5.	≤0.3	--	--	--	≤1.
I	≤0.04	--	--	--	1.	≤0.1	--	--	--	3.
Hg	<0.06	<1.6	--	--	<2.	<0.1	<0.8	--	--	<2.
Tl	<0.03	--	--	--	≤0.3	<0.03	--	--	--	1.
Pb	2,000.	600.	10,000.	2,600.	3,000.	1,000.	2,400.	5,430.	1,200	3,000.
Bi	2.	--	--	--	3.	0.2	--	--	--	1.

Element	Sample Designation: M 000 408 (Ash) SSMS	OES	Chem	XRF
Li	20.	--	--	--
B	20.	30.	--	--
Na	5,000.	1,200.	12,500.	--
Mg	2,000.	1,500.	1,920.	--
Al	2,000.	3,000.	--	3,200.
Si	6,000.	6,000.	--	10,200.
K	4,000.	1,500.	1,920,	2,300.
Ca	10,000.	40,000.	16,600.	17,000.
Sc	1.	--	--	--
Ti	600.	300.	--	320.
V	40.	12.	--	50.
Cr	60.	15.	--	--
Mn	100.	60.	--	--
Fe	5,000.	1,500.	6,900.	8,200.
Co	10.	3.	--	--
Ni	50.	15.	--	--
Cu	2,000.	300.	3,200.	3,100.
Zn	1,000.	600.	3,840.	3,800.
Ge	10.	--	--	--
Rb	40.	--	--	--
Sr	100.	--	--	--
Y	2.	--	--	--
Zr	6.	12.	--	--
Nb	2.	--	--	--
Mo	10.	3.	--	--
Ru	<0.04	--	--	--
Rh	<0.1	--	--	--
Pd	<0.4	--	--	--
Ag	20.	30.	--	--
Cd	10.	--		

Element	Sample Designation: M 000 408 (Ash) SSMS	OES
In	≤2.	--
Sn	500.	30.(a)
Sb	10.	--
Cs	2.	--
Ba	200.	50.
La	2.	--
Ce	5.	--
Pr	1.	--
Nd	3.	--
Sm	0.6	--
Eu	<0.4	--
Gd	<1.	--
Tb	<0.2	--
Dy	<0.6	--
Ho	<0.2	--
Er	<0.6	--
Tm	<0.1	--
Yb	<0.4	--
Lu	<0.2	--
Hf	<0.2	--
Ta	<0.3	--
W	0.6	--
Re	<0.06	--
Os	<0.06	--
Ir	<0.03	--
Pt	<0.1	--
Au	<0.03	--
Th	1.	--
U	2.	--

Element	Sample Designation: M 000 409 (Ash) OES	Chem	XRF
Na	2,430.	15,900.	--
Mg	3,240.	2,350.	--
Al	570.	--	2,000.
Si	2,200.	--	13,500.
K	3,240.	1,460.	2,300.
Ca	17,100.	16,200.	18,500.
Ti	400.	--	485.
V	25.	--	45.
Cr	32.	--	--
Mn	80.	--	--
Fe	5,670.	7,940.	8,100.
Co	16.	--	--
Ni	32.	--	--
Cu	320.	810.	530.
Zn	570.	1,050.	640.
Zr	6.	--	--
Mo	40.	--	--
Ag	0.9	--	--
Sn	32.	--	70.
Ba	80.	--	--

(a) XRF result: 60.

TABLE A-5. ANALYSIS OF AIR PARTICULATES ON MILLIPORE - WASHINGTON

(Nanograms/M^3)

Element	Sample Designation: M 000 406 (Ash) SSMS	OES	Chem	XRF	M 000 406 (C_6H_6 Wash) SSMS	M 000 407 (Ash) SSMS	OES	Chem	XRF	M 000 407 (C_6H_6 Wash) SSMS
Be	0.1	0.02	--	--	0.2	0.2	0.2	--	--	0.3
F	20.	--	--	--	100.	100.	--	--	--	100.
P	30.	--	--	30.	--	10.	--	--	--	--
S	1,000.	--	--	3,800.	6,000.	3,000.	--	--	35.	10,000.
Cl	50.	--	--	<4.	100.	200.	--	--	7,000.	300.
Ga	3.	--	--	--	20.	10.	--	--	--	10.
As	10.	--	--	--	150.	10.	--	--	--	20.
Se	3.	--	--	--	6.	6.	--	--	--	20.
Br	10.	--	--	--	150.	20.	--	--	--	100.
Te	0.2	--	--	--	0.4	0.2	--	--	--	0.4
I	≤0.01	--	--	--	4.	≤0.02	--	--	--	4.
Hg	<0.02	<0.5(T)	--	--	<3.	<0.04	<0.6(T)	--	--	<1.
Tl	0.02	--	--	--	<0.2	≤0.02	--	--	--	<1.
Pb	1,500.	1,500.	2,810.	2,900.	2,000.	3,000.	3,000.	3,900.	4,200.	5,000.
Bi	0.2	--	--	--	0.4	1.	--	--	--	<3.

Element	Sample Designation: M 000 406 (Ash) SSMS	OES	Chem	XRF	Element	M 000 406 (Ash) SSMS	OES	Element	M 000 407 (Ash) OES	Chem	XRF
Li	3.	--	--	--	Cd	0.3	--	Na	580.	4,870.	--
B	3.	10.	--	--	In	<0.5	--	Mg	2,030.	1,800.	--
Na	1,000.	200.	1,510.	--	Sn	10.(a)	5.	Al	3,500.	--	3,300.
Mg	1,000.	1,000.	830.	--	Sb	2.	--	Si	9,800.	--	11,300.
Al	1,000.	1,700.	--	2,000.	Cs	3.	--	K	2,030.	930.	1,600.
Si	3,000.	4,400.	--	7,000.	Ba	150.	35.	Ca	3,500.	4,600.	4,800.
K	2,000.	1,000.	780.	1,150.	La	4.	--	Ti	290.	--	320.
Ca	6,000.	1,700.	3,020.	3,700.	Ce	3.	--	V	170.	--	200.
Sc	1.	--	--	--	Pr	1.	--	Cr	25.	--	--
Ti	300.	150.	--	230.	Nd	3.	--	Mn	50.	--	--
V	100.	100.	--	180.	Sm	0.5	--	Fe	2,030.	3,950.	4,500.
Cr	10.	15.	--	--	Eu	0.1	--	Co	12.	--	--
Mn	50.	35.	--	--	Gd	0.3	--	Ni	60.	--	--
Fe	1,500.	1,700.	2,550.	3,200.	Tb	0.05	--	Cu	170.	640.	460.
Co	5.	10.	--	--	Dy	0.2	--	Zn	170.	460.	460.
Ni	40.	35.	--	--	Ho	0.03	--	Zr	12.	--	--
Cu	150.	100.	570.	430.	Tm	<0.03	--	Mo	2.	--	--
Zn	50.	200.	860.	300.	Yb	<0.3	--	Ag	1.	--	--
Ge	3.	--	--	--	Lu	<0.02	--	Sn	12.	--	8.
Rb	10.	--	--	--	Hf	<0.05	--	Ba	35.	--	--
Sr	100.	--	--	--	Ta	≤0.05	--				
Y	1.	--	--	--	W	0.1	--				
Zr	2.	5.	--	--	Re	<0.01	--				
Nb	0.3	--	--	--	Os	<0.02	--				
Mo	1.	2.	--	--	Ir	<0.01	--				
Ru	<0.01	--	--	--	Pt	<0.02	--				
Rh	<0.03	--	--	--	Au	<0.02	--				
Pd	<0.1	--	--	--	Th	0.05	--				
Ag	0.6	0.5	--	--	U	0.05	--				

(a) SSMS results on C_6H_6 Wash: Sn, 60.; Ba, 50. XRF result on ash: Sn, 13.

TABLE A-6. ANALYSIS OF AIR PARTICULATES ON MILLIPORE - CHICAGO

(Nanagrams/M^3)

Element	Sample Designation: M 000 414 (Ash) SSMS	OES	Chem	XRF	M 000 415 (Ash) SSMS	OES	Chem	XRF
Be	<0.1	<3.	--	--	0.3	<6.	--	--
F	30.	--	--	--	150.	--	--	--
P	60.	--	--	60.	100.	--	--	300.
S	1,000.	--	--	5,400.	2,000.	--	--	15,500.
Cl	2,000.	--	--	10,000.	400.	--	--	3,600.
Ga	6.	--	--	--	10.	--	--	--
As	60.	--	--	--	60.	--	--	--
Se	2.	--	--	--	6.	--	--	--
Br	100.	--	--	--	200.	--	--	--
Te	≤0.2	--	--	--	≤0.2	--	--	--
I	≤0.7	--	--	--	<0.6	--	--	--
Hg	<0.04	--	--	--	<0.1	--	--	--
Tl	≤0.01	--	--	--	0.04	--	--	--
Pb	1,500.	3,000.	4,570.	3,600.	3,000.	4,200.	10,040.	5,500.
Bi	1.	--	--	--	3.	--	--	--

Element	Sample Designation: M 000 414 (Ash) SSMS	OES	Chem	XRF	Element	M 000 414 (Ash) SSMS	OES	Chem	XRF	Element	M 000 415 (Ash) OES	Chem	XRF
Li	2.	--	--	--	In	<1.	--	--	--	Na	2,100.	6,430.	--
B	3.	10.	--	--	Sn	40.	20.	--	10.	Mg	10,500.	13,520.	--
Na	3,000.	3,000.	8,600.	--	Sb	8.	--	--	--	Al	6,000.	--	5,400.
Mg	4,000.	5,200.	5,290.	Cs	Cs	0.7	--	--	--	Si	30,000.	--	18,500.
Al	1,500.	3,000.	--	1,850.	Ba	60.	30.	--	--	K	1,500.	1,260.	3,400.
Si	5,000.	15,000.	--	5,500.	La	5.	--	--	--	Ca	21,000.	25,900.	30,000.
K	3,000.	1,000.	590.	1,200.	Ce	7.	--	--	--	Ti	600.	--	200.
Ca	10,000.	10,000.	10,420.	12,000.	Pr	2.	--	--	--	V	60.	--	30.
Sc	3.	--	--	--	Nd	5.	--	--	--	Cr	40.	--	--
Ti	300.	300.	--	≤2.	Sm	2.	--	--	--	Ti	600.	--	200.
V	200.	100.	--	40.	Eu	0.3	--	--	--	V	60.	--	30.
Cr	20.	20.	--	--	Gd	2.	--	--	--	Cr	40.	--	--
Mn	100.	100.	--	--	Tb	≤0.1	--	--	--	Mn	200.	--	--
Fe	2,000.	5,200.	3,520.	4,500.	Dy	0.3	--	--	--	Fe	10,500.	8,050.	10,300.
Co	10.	--	--	--	Ho	0.1	--	--	--	Ni	120.	--	--
Ni	20.	60.	--	--	Er	≤0.2	--	--	--	Cu	600.	960.	900.
Cu	300.	300.	400.	430.	Tm	≤0.1	--	--	--	Zn	600.	1,080.	800.
Zn	70.	300.	560.	500.	Yb	≤0.5	--	--	--	Zr	<20.	--	--
Ge	7.	--	--	--	Lu	<0.1	--	--	--	Mo	<6.	--	--
Rb	20.	--	--	--	Hf	<0.3	--	--	--	Sn	40.	--	2.
Sr	40.	--	--	--	Ta	≤0.1	--	--	--	Ba	60.	--	--
Y	1.	--	--	--	W	1.	--	--	--				
Zr	4.	<10.	--	--	Re	<0.05	--	--	--				
Nb	0.5	--	--	--	Os	<0.04	--	--	--				
Mo	3.	<3.	--	--	Ir	<0.02	--	--	--				
Ru	<1.	--	--	--	Pt	<0.04	--	--	--				
Rh	<0.06	--	--	--	Au	<0.1	--	--	--				
Pd	<0.3	--	--	--	Th	0.4	--	--	--				
Ag	2.	--	--	--	U	0.2	--	--	--				
Cd	3.	--	--	--									

TABLE A-7. ANALYSIS OF AIR PARTICULATES ON MILLIPORE - PHILADELPHIA

(Nanograms/M^3)

Element	Sample Designation: M 000 419 (Ash) SSMS	OES	Chem	XRF	M 000 418 (Ash) SSMS	OES	Chem	XRF
Be	0.1	<4.	--	--	0.04	<4.	--	--
F	40.	--	--	--	10.	--	--	--
P	60.	--	--	50.	60.	--	--	330.
S	1,000.	--	--	3,400.	600.	--	--	3,100.
Cl	4.	--	--	<4.	10.	--	--	10.
Ga	6.	--	--	--	4.	--	--	--
As	10.	--	--	--	2.	--	--	--
Se	2.	--	--	--	2.	--	--	--
Br	20.	--	--	--	5.	--	--	--
Te	≤0.1	--	--	--	≤0.1	--	--	--
I	0.01	--	--	--	≤0.01	--	--	--
Hg	<0.03	--	--	--	<0.02	--	--	--
Tl	0.04	--	--	--	0.04	--	--	--
Pb	1,500.	2,000.	2,060.	2,000.	2,000.	1,900.	2,380.	2,400
Bi	0.6	--	--	--	1.	--	--	--

Element	Sample Designation: M 000 419 (Ash) SSMS	OES	Chem	XRF	Element	M 000 419 (Ash) SSMS	OES	Chem	XRF	Element	M 000 418 (Ash) OES	Chem	XRF
Li	2.	--	--	--	In	<1.	--	--	--	Na	630.	920.	--
B	2.	8.	--	--	Sn	70.	40.	--	30.	Mg	3,100.	3,250.	--
Na	1,000.	480.	820.	--	Sb	60.	--	--	--	Al	3,100.	--	1,900.
Mg	5,000.	4,000.	5,240.	--	Cs	0.4	--	--	--	Si	12,500.	--	5,800.
Al	2,000.	4,800.	--	2,500.	Ba	30.	40.	--	--	K	630.	500.	1,000.
Si	10,000.	19,000.	--	9,000.	La	20.	--	--	--	Ca	4,200.	6,000.	5,400.
K	1,000.	1,000.	620.	1,600.	Ce	20.	--	--	--	Ti	330.	--	170.
Ca	5,000.	6,800.	9,620.	8,000.	Pr	4.	--	--	--	V	210.	--	17.
Sc	10.	--	--	--	Nd	7.	--	--	--	Cr	25.	--	--
Ti	600.	480.	--	250.	Sm	1.	--	--	--	Mn	130.	--	--
V	250.	280.	--	200.	Eu	0.2	--	--	--	Fe	3,100.	2,830.	2,900.
Cr	60.	35.	--	--	Gd	0.6	--	--	--	Ni	80.	--	--
Mn	200.	160.	--	--	Tb	0.2	--	--	--	Cu	130.	170.	590.
Fe	6,000.	4,000.	3,800.	4,050.	Dy	0.6	--	--	--	Zn	210.	830.	550.
Co	20.	--	--	--	Ho	0.1	--	--	--	Zr	12.	--	--
Ni	100.	80.	--	--	Er	0.3	--	--	--	Mo	<4.	--	--
Cu	200.	80.	160.	350.	Tm	0.06	--	--	--	Sn	25.	--	20.
Zn	500.	280.	820.	500.	Yb	0.3	--	--	--	Ba	35.	--	--
Ge	<0.4	--	--	--	Lu	≤0.04	--	--	--				
Rb	20.	--	--	--	Hf	0.2	--	--	--				
Sr	40.	--	--	--	Ta	≤0.2	--	--	--				
Y	2.	--	--	--	W	1.	--	--	--				
Zr	10.	20.	--	--	Re	<0.02	--	--	--				
Nb	0.3	--	--	--	Os	<0.03	--	--	--				
Mo	2.	<4.	--	--	Ir	<0.06	--	--	--				
Ru	<0.03	--	--	--	Pt	<0.03	--	--	--				
Rh	<0.01	--	--	--	Au	<0.06	--	--	--				
Pd	<0.3	--	--	--	Th	0.2	--	--	--				
Ag	0.6	--	--	--	U	0.2	--	--	--				
Cd	1.	--	--	--									

TABLE A-8. ANALYSIS OF AIR PARTICULATES ON GLASS - CINCINNATI

(Nanograms/M^3)

Element	Sample Designation: G 000 6978 C_6H_6 Wash SSMS	G 000 6978 C_6H_6 Wash OES	G 000 6978 Crushed SSMS	G 000 6978 Crushed Chem	G 000 6977 C_6H_6 Wash SSMS	G 000 6977 C_6H_6 Wash OES	G 000 6977 Crushed SSMS	G 000 6966 C_6H_6 Wash SSMS	G 000 6966 C_6H_6 Wash OES	G 000 6966 Crushed SSMS	G 002 C_6H_6 Wash SSMS	G 002 C_6H_6 Wash OES	G 002 Crushed SSMS	G 001 C_6H_6 Wash SSMS	G 001 C_6H_6 Wash OES	G 001 Crushed SSMS
Be	0.2	0.2	(a)	--	0.1	0.2	(a)	0.1	0.3	(a)	0.4	0.3	(a)	0.2	0.3	(a)
F	50.	--	(a)	<400. (b)	20.	--	(a)	30.	--	(a)	300.	--	(a)	50.	--	(a)
P	50.	--	(a)	--	300.	--	(a)	50.	--	(a)	50.	--	(a)	100.	--	(a)
S	3000.	--	3000.	4400. (b)	7000.	--	7000.	7000.	--	7000.	7000.	--	7000.	2000.	--	2000.
Cl	5000.	--	5000.	5330. (b)	3000.	--	3000.	1000.	--	1000.	1000.	--	1000.	400.	--	400.
Ga	5.	--	5.	--	10.	--	10.	10.	--	5.	10.	--	10.	3.	--	3.
As	20.	--	20.	--	40.	--	20.	70.	--	40.	20.	--	20.	40.	--	40.
Se	7.	--	7.	--	15.	--	10.	10.	--	10.	10.	--	10	15.	--	10.
Br	200.	--	200.	--	200.	--	200.	400.	--	400.	200.	--	200.	200.	--	200.
Te	≤0.6	--	≤0.6	--	<0.6	--	≤2.	≤1.	--	≤0.3	≤1.	--	<0.4	≤1.	--	≤1.
I	2.	--	2.	--	2.	--	2.	2.	--	2.	1.	--	1.	0.6	--	2.
Hg	<1.	--	<1.	--	<0.4	--	<3.	≤0.4	--	≤1.	<1.	--	<1.	<1.	--	<0.4
Tl	<0.4	--	<0.4	--	<0.6	--	<2.	<0.2	--	<0.6	<0.4	--	<0.4	<0.6	--	<0.2
Pb	300.	900.	300.	--	400.	300.	400.	600.	1800.	600.	400.	900.	400.	--	--	--

Element	Sample Designation: G 000 6978 C_6H_6 Wash SSMS	G 000 6978 C_6H_6 Wash OES	Element	G 000 6978 C_6H_6 Wash SSMS	G 000 6978 C_6H_6 Wash OES
Li	5.	--	In	<6.	--
B	30.	30.	Sn	50.	40.
Na	2000.	1400.	Sb	6.	--
Mg	800.	1400.	Cs	0.6	--
Al	2500.	2500.	Ba	20.	60.
Si	3000.	7000.	La	1.	--
K	1000.	1200.	Ce	1.	--
Ca	2000.	4000.	Pr	1.	--
Sc	1.	--	Nd	2.	--
Ti	100.	200.	Sm	≤1.	--
V	3.	2.	Eu	<0.4	--
Cr	2.	4.	Gd	<1.	--
Mn	100.	40.	Tb	<0.3	--
Fe	1000.	900.	Dy	<1.	--
Co	2.	2.	Ho	<0.3	--
Ni	25.	6.	Er	<1.	--
Cu	150.	60.	Tm	<0.3	--
Zn	300.	400.	Yb	<1.	--
Ge	4.	--	Lu	<0.3	--
Rb	4.	--	Hf	<1.	--
Sr	2.	--	Ta	<3.	--
Y	4.	--	W	<1.	--
Zr	≤1.	4.	Re	<0.6	--
Nb	0.5	--	Os	<1.	--
Mo	3.	--	Ir	<0.6	--
Ru	<0.6	--	Pt	<1.	--
Rh	<0.6	--	Au	<1.	--
Pd	<1.	--	Bi	1.	--
Ag	<1.	0.6	Th	<0.4 (c)	--
Cd	6.	--	U	<0.4 (c)	--

(a) Too high in blank to make estimate.
(b) On residue after C_6H_6 extraction.
(c) SSMS results on crushed: Th, 0.2; U, 0.2.

TABLE A-9. ANALYSIS OF AIR PARTICULATES ON GLASS - DENVER

(Nanograms/M^3)

Element	Sample Designation: G 000 6981 C_6H_6 Wash SSMS	G 000 6981 C_6H_6 Wash OES	G 000 6981 Crushed SSMS	G 000 6981 Crushed Chem	G 000 6982 C_6H_6 Wash SSMS	G 000 6982 C_6H_6 Wash OES	G 000 6982 Crushed SSMS	G 000 6982 Crushed Chem
Be	0.3	0.04	(a)	--	<0.1	0.04	(a)	--
F	200.	--	(a)	<400.(b)	700.	--	(a)	--
P	100.	--	(a)	--	200.	--	(a)	--
S	1,000.	--	1,000.	1,700.(b)	2,500.	--	2,000.	6,980.(b)
Cl	2,000.	--	2,000.	9,030.(b)	1,500.	--	2,000.	6,400.(b)
Ga	5.	--	≤3.	--	<3.	--	3.	--
As	10.	--	≤5.	--	10.	--	10.	--
Se	≤1.	--	≤1.	--	≤10.	--	10.	--
Br	200.	--	200.	--	600.	--	600.	--
Te	≤0.3	--	<0.3	--	≤1.	--	≤1.	--
I	2.	--	1.	--	5.	--	5.	--
Hg	<1.	--	<1.	--	<5.	--	<2.	--
Tl	<0.6	--	<0.3	--	<2.	--	<1.	--
Pb	1,000.	1,500.	400.	--	5,000.	4,000.	2,000.	--
Bi	1.	--	1.	--	--	--	--	--

Element	Sample Designation: G 000 6981 C_6H_6 Wash SSMS	G 000 6981 C_6H_6 Wash OES	Element	G 000 6981 C_6H_6 Wash SSMS	G 000 6981 C_6H_6 Wash OES	Element	G 000 6981 C_6H_6 Wash SSMS
Li	10.	--	Sr	70.	--	Eu	<2.
B	30.	40.	Y	3.	--	Gd	<3.
Na	high	3,000.	Zr	10.	15.	Tb	<1.
Mg	1,500.	760.	Nb	3.	--	Dy	<3.
Al	5,000.	7,200.	Mo	4.	8.	Ho	<0.6
Si	high	--	Ru	<0.5	--	Er	<0.5
K	4,000.	5,700.	Rh	<0.2	--	Tm	<0.2
Ca	7,000.	4,200.	Pd	<2.	--	Yb	<1.
Sc	3.	--	Ag	<1.	1.	Lu	<0.6
Ti	500.	380.	Cd	2.	--	Hf	<1.
V	20.	8.	In	<10.	--	Ta	<0.6
Cr	15.	15.	Sn	10.	8.	W	2.
Mn	30.	80.	Sb	4.	--	Re	<0.6
Fe	5,000.	3,000.	Cs	1.	--	Os	<1.
Co	5.	1.	Ba	700.	380.	Ir	<0.6
Ni	50.	15.	La	10.	--	Pt	<1.
Cu	500.	380.	Ce	15.	--	Au	<0.4
Zn	100.	150.	Pr	3.	--	Th	<0.2
Ge	5.	--	Nd	10.	--	U	<1.
Rb	70.	--	Sm	2.	--		

(a) Too high in blank to make estimate.
(b) On residue after C_6H_6 extraction.

TABLE A-10. ANALYSIS OF AIR PARTICULATE ON GLASS - ST. LOUIS

(Nanograms/M^3)

Element	Sample Designation: G 000 6985 C_6H_6 Wash SSMS	C_6H_6 Wash OES	Crushed SSMS	Crushed Chem	G 000 6986 C_6H_6 Wash SSMS	C_6H_6 Wash OES	Crushed SSMS	Crushed Chem
Be	0.2	0.1	(a)	--	0.3	0.1	(a)	--
F	200.	--	(a)	<400. (b)	200.	--	(a)	--
P	200.	--	(a)	--	100.	--	(a)	--
S	6,000.	--	6,000.	8,700. (b)	500.	--	500.	6,290. (b)
Cl	1,500.	--	1,500.	13,200. (b)	500.	--	500.	15,300. (b)
Ga	3.	--	≤3.	--	1.	--	1.	--
As	50.	--	50.	--	5.	--	5.	--
Se	10.	--	5.	--	2.	--	2.	--
Br	200.	--	200.	--	100.	--	100.	--
Te	6.	--	6.	--	≤0.3	--	≤0.3	--
I	3.	--	3.	--	1.	--	1.	--
Hg	<1.	--	<0.4	--	<2.	--	<1.	--
Tl	<2.	--	<0.2	--	≤0.5	--	≤0.5	--
Pb	100.	560.	400.	--	500.	600.	300.	--
Bi	3.	--	1.	--	--	--	--	--

Element	Sample Designation: G 000 6985 C_6H_6 Wash SSMS	C_6H_6 Wash OES	Element	G 000 6985 C_6H_6 Wash SSMS	C_6H_6 Wash OES
Li	5.	--	Cd	3.	--
B	30.	30.	In	<2.	--
F	200.	--	Sn	60.	20.
Na	3,000.	800.	Sb	5.	--
Mg	400.	560.	Cs	1.	--
Al	3,000.	1,400.	Ba	100.	50.
Si	5,000.	4,000.	La	2.	--
K	3,000.	800.	Ce	2.	--
Ca	10,000.	4,000.	Pr	0.7	--
Sc	1.	--	Nd	2.	--
Ti	200.	140.	Sm	<0.6	--
V	3.	3.	Eu	<2.	--
Cr	30.	14.	Gd	<0.3	--
Mn	100.	30.	Tb	<0.1	--
Fe	2,000.	800.	Dy	<0.5	--
Co	3.	1.	Ho	<1.	--
Ni	30.	14.	Er	<0.1	--
Cu	1,000.	300.	Tm	<0.1	--
Zn	600.	560.	Yb	<0.5	--
Ge	3.	--	Lu	<0.1	--
Rb	5.	--	Hf	<0.3	--
Sr	10.	--	Ta	<2.	--
Y	2.	--	W	≤0.3	--
Zr	5.	--	Re	<0.2	--
Nb	0.3	--	Os	<0.3	--
Mo	3.	1.4	Ir	<0.4	--
Ru	<0.2	--	Pt	<0.2	--
Rh	<0.2	--	Au	<0.2	--
Pd	<1.	--	Th	<1.	--
Ag	6.	2.	U	<0.5	--

(a) Too high in blank to make estimate.
(b) On residue after C_6H_6 extraction.

TABLE A-11. ANALYSIS OF AIR PARTICULATE ON GLASS - WASHINGTON

(Nanograms/M^3)

Element	Sample Designation: G 000 6990 C_6H_6 Wash SSMS	G 000 6990 C_6H_6 Wash OES	G 000 6990 Crushed SSMS	G 000 6990 Crushed Chem	G 000 6989 C_6H_6 Wash SSMS	G 000 6989 C_6H_6 Wash OES	G 000 6989 Crushed SSMS	G 000 6989 Crushed Chem
Be	0.1	0.2	--	--	0.01	0.04	--	--
F	500.	--	(a)	--	100.	--	(a)	<400. (b)
P	100.	--	(a)	--	100.	--	(a)	--
S	7000.	--	7000.	6760. (b)	2000.	--	2000.	4400. (b)
Cl	1000.	--	300.	1670. (b)	300.	--	300.	270. (b)
Ga	3.	--	≤3.	--	1.	--	1.	--
As	50.	--	20.	--	10.	--	10.	--
Se	10.	--	10.	--	≤2.	--	5.	--
Br	300.	--	100.	--	200.	--	300.	--
Te	≤0.6	--	≤0.6	--	≤0.6	--	≤0.6	--
I	10.	--	4.	--	3.	--	3.	--
Hg	<1.	--	<1.	--	≤2.	--	<0.5	--
Tl	<2.	--	<0.5	--	<0.5	--	<0.2	--
Pb	2000.	1200.	200.	--	100.	1500.	1000.	--
Bi	5.	--	1.	--	--	--	--	--

Element	Sample Designation: G 000 6990 C_6H_6 Wash SSMS	G 000 6990 C_6H_6 Wash OES	Element	G 000 6990 C_6H_6 Wash SSMS	G 000 6990 C_6H_6 Wash OES
Li	4.	--	Cd	--	--
B	10.	25.	In	<1.	--
Na	5000.	900.	Sn	30.	10.
Mg	2000.	900.	Sb	4.	--
Al	1000.	2000.	Cs	<0.1	--
Si	6000.	8000.	Ba	200.	90.
K	4000.	1400.	La	4.	--
Ca	4000.	2000.	Ce	6.	--
Sc	<2.	--	Pr	0.6	--
Ti	200.	200.	Nd	<2.	--
V	200.	200.	Sm	≤1.	--
Cr	20.	14.	Eu	<1.	--
Mn	100.	45.	Gd	<1.	--
Fe	2000.	900.	Tb	<0.2	--
Co	4.	9.	Dy	<0.6	--
Ni	100.	100.	Ho	<1.	--
Cu	400.	360.	Er	<0.3	--
Zn	500.	360.	Tm	<0.3	--
Ge	5.	--	Yb	<0.3	--
Rb	4.	--	Lu	<0.2	--
Sr	4.	--	Hf	<0.5	--
Y	1.	--	Ta	<1.	--
Zr	4.	9.	W	<1.	--
Nb	<0.6	--	Re	<0.5	--
Mo	2.	2.	Os	<1.	--
Ru	<4.	--	Ir	<0.5	--
Rh	<0.6	--	Pt	<1.	--
Pd	<3.	--	Au	<1.	--
Ag	<1.	1.	Th	<4.	--
			U	<4.	--

(a) Too high in blank to make estimate.
(b) On residue after C_6H_6 extraction.

TABLE A-12. ANALYSIS OF AIR PARTICULATE ON GLASS - CHICAGO

(Nanograms/M^3)

Element	Sample Designation[a] G 000 6979 SSMS	G 000 6979 Chem	G 906 280 SSMS	G 906 280 Chem	G 686 900 SSMS	G 686 900 Chem
Be	(b)	--	(b)	--	(b)	--
F	(b)	<400.(c)	(b)	940.(c)	(b)	<400.(c)
P	100.	--	100.	--	300.	--
S	3,000.	--	3,000.	7,000.(c)	1,000.	--
Cl	3,000.	10,690.(c)	500.	9,870.(c)	2,000.	7,930.(c)
Ga	10.	--	20.	--	(a)	--
As	100.	--	100.	--	70.	--
Se	≤5.	--	≤10.	--	≤3.	--
Br	700.	--	500.	--	300.	--
Te	≤0.2	--	≤0.6	--	<0.6	--
I	5.	--	4.	--	1.	--
Hg	<1.	--	≤0.5	--	<1.	--
Tl	<0.6	--	≤0.5	--	<0.3	--
Pb	5,000.	--	4,000.	--	2,000.	--
Bi	1.	--	4.	--	0.6	--

(a) Samples were crushed.
(b) Too in blank to make estimate.
(c) On residue after C_6H_6 extraction.

TABLE A-13. ANALYSIS OF AIR PARTICULATE ON GLASS - PHILADELPHIA

(Nanograms/M^3)

Element	Sample Designation[a] G 000 6967 SSMS	G 000 6967 Chem	G 000 6968 SSMS	G 000 6968 Chem
Be	(b)	--	(b)	--
F	(b)	<400.(c)	(b)	<400.(c)
P	100.	--	30.	--
S	1500.	--	2500.	5200.(c)
Cl	150.	680.(c)	150.	190.(c)
Ga	(a)	--	(a)	--
As	(a)	--	10.	--
Se	≤10.	--	≤5.	--
Br	500.	--	150.	--
Te	<1.	--	<0.3	--
I	5.	--	1.	--
Hg	<2.	--	<0.5	--
Tl	≤1.	--	<0.3	--
Pb	3000.	--	1000.	--
Bi	4.	--	0.2	--

(a) Samples were crushed.
(b) Too high in blank to make estimate.
(c) On residue after C_6H_6 extraction.

TABLE A-14. ANALYSIS OF AIR PARTICULES ON GLASS FOR HYDROGEN, CARBON, AND NITROGEN

(Nanograms/M^3)

Sample Designation	City	As Received			Benzene Insoluble Phase		
		Hydrogen	Carbon	Nitrogen	Hydrogen	Carbon	Nitrogen
G 000 6978	Cincinnati	3,100.	30,200.	2,760.	1,610.	16,900.	2,430.
G 000 6985	St. Louis	7,370.	62,000.	6,020.	3,320.	28,400.	4,620.
G 000 6989	Washington	2,950.	27,800.	2,390.	1,820.	17,300.	2,120.
G 000 6968	Philadelphia	4,110.	30,500.	4,540.	2,190.	15,300.	3,050.
G 000 6981	Denver	4,910.	44,000.	2,490.	2,780.	30,500.	2,850.
G 906 280	Chicago	11,600.	111,000.	9,730.	4,710.	50,100.	7,830.

Discussion of Data. The data in the tables should be self-explanatory. There are no ready explanations for the wide variations in some of the values by the various techniques. Synthetic standards were made and run for each method except the mass spectrographic. Where spreads occurred the original data were reexamined for obvious errors, and a few errors were spotted and corrected. On the positive side, a large number of the values agree better than the estimated accuracy of the method. This probably means that the stated accuracies for the techniques are conservative. High concentration elements are not easily determined by mass spectrography because the isotopic lines, especially for monoisotopic elements, are too heavy to read accurately. Therefore, in those instances where the SSMS data do not agree with other values, the SSMS results should be ignored.

On the basis of experience and intuition, the expected ranking of accuracy for each technique and method is roughly in this order:

Chemical and XRF
Optical emission on Millipore
Mass spectrography on ashed Millipore
Mass spectrography on C_6H_6 Wash of Millipore
Mass spectrography on C_6H_6 Wash of glass
Optical emission on glass
Mass spectrography on crushed (ground) glass.

If these data are to be published later as an HEW document, it might be best to pick a single value for each element in each filter rather than to give cross-check data. The thrust of such a publication should be the presentation of values, not a comparison of techniques.

Light (Optical) and Electron Microscopy

Specimen Preparation

Light Microscopy. In the case of light microscopy, benzene extraction was carried out in a series of petri dishes containing copper screen platforms supported by bent glass rods. The level of benzene in each dish was adjusted so that the holes in the screen were filled with benzene. A piece of lens tissue was numbered with the sample number and a piece of membrane filter bearing the collected particles was placed particle-side-up on the lens tissue and together they were placed on the screen platform in the petri dish, covered, and allowed to remain 2 hours. Extraction was carried out for 2 hours in each of three petri dishes.

One of the specimens for light microscopy was prepared by scraping particles off the membrane filters onto microscope slides and dispersing the particles in balsam beneath a coverslip. The particles were too heavily deposited on the filter to examine directly. Even in these diluted preparations, the relative abundance of particles too small to be resolved by light microscopy was so high that many of the larger particles were not clearly visible. To avoid thin masking by the smaller particles, centrifugation was employed to separate and concentrate the larger particles to make specimen preparations for photomicrography. All the photomicrographs in this report were made of these coarse particle fractions.

Electron Microscopy. Benzene extraction of the samples prior to electron microscopy was done in a manner different from that for light microscopy, primarily because specimen preparation for electron microscopy involved suspending the collected particles in a liquid and redepositing them on another Millipore filter. The redeposition was done to obtain a more thinly dispersed preparation which could be examined electron microscopically. The liquid chosen to suspend the particles was benzene since benzene-extraction was desired and benzene does not attack the Millipore filter. The following steps were involved in specimen preparation for electron microscopy:

(1) Glassware (beakers, filtering apparatus, etc.) was cleaned with aqua regia, rinsed with deionized water, dried, and finally rinsed with benzene.

(2) The collection filter was cut into a square 0.5 x 0.5 cm which was then cut in half to result in an area of 0.125 cm^2.

(3) This filter area was placed in 20 ml of benzene and treated ultrasonically to remove particles from the filter and to suspend them in benzene.

(4) While the particles were kept in suspension by ultrasonification, the benzene was aspirated from the container and filtered through a Millipore filter area 17 mm in diameter.

(5) After the filter was dry, carbon was vapor deposited over the particles and the Millipore filter was dissolved to leave a carbon film holding the particles.

(6) The carbon film and particles were picked up on an electron-microscope support grid and examined in the electron microscope.

The electron micrographs shown in this report were made from the preceding type of preparation. In addition to the images of the air-pollution particles, the electron micrographs show the replica of the Millipore filter structure in the background.

Results of Microscopy

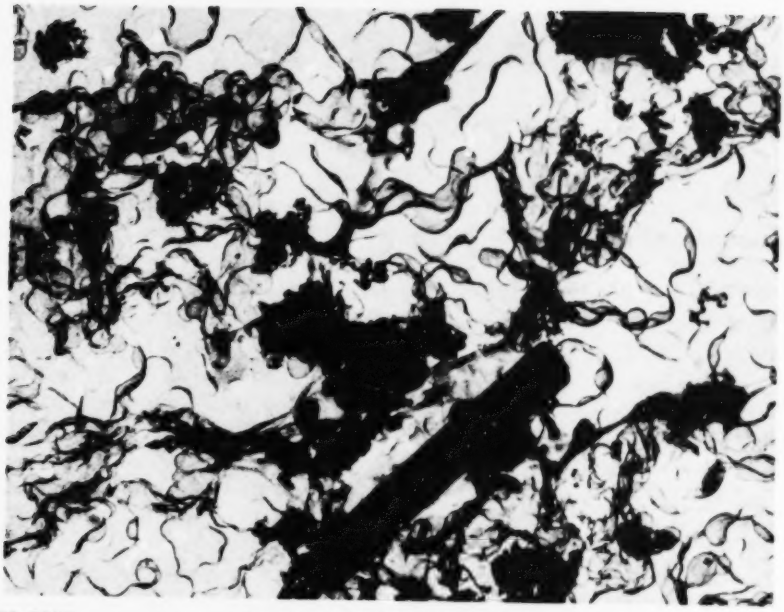
In general there are several very prevalent airborne materials collected in all six cities (Washington, Denver, Cincinnati, Chicago, Philadelphia, and St. Louis). These materials are: flyash, carbon black, quartz, and iron rust. Flyash (particles created by combustion) is often identifiable because the spherical structure indicates that it was liquid at one point when airborne. Flyash appears to have many compositions, ranging from carbonaceous to siliceous, and to be the most prevalent material in all collected samples. The diameter of flyash particles ranges from approximately 15.0 μ down to submicron sizes, $<0.2\ \mu$. In addition, electron microscopy revealed particles down to 250 A. This clearly demonstrates the effectiveness of 3-μ pore-size membrane (Millipore) filters in trapping much smaller particles than does the nominal pore size.

Soot or carbon black is also very prevalent as a particulate product of combustion and might fit the definition for flyash; however, it is felt that the chained structure characteristic of finely divided carbon black places it in a unique category. It is found in large quantities in all samples and, because of various origins and large surface area, may carry very valuable chemical information as to air pollutants, gaseous as well as particulate, unique to the collection site. In addition to the chained carbon black, there are relatively large ($\sim$10.0 to 20.0 μ) roughly spherical oil soot particles. This oil soot is especially prevalent in the Philadelphia sample, M 000 414.

Quartz is not nearly as prevalent in air samples as are flyash and soot, but does comprise a significant fraction which is markedly greater in the Denver sample; consequently, the ratio of quartz to carbon black is also greater. The observed absolute quantity of carbon black per cubic meter is less in the Denver samples, but the elemental carbon analysis is quite high. There are other crystalline particulates, in addition to quartz, present in all samples. It is anticipated that some of these will be identified with the aid of X-ray diffraction and the electron microprobe during the new contract period.

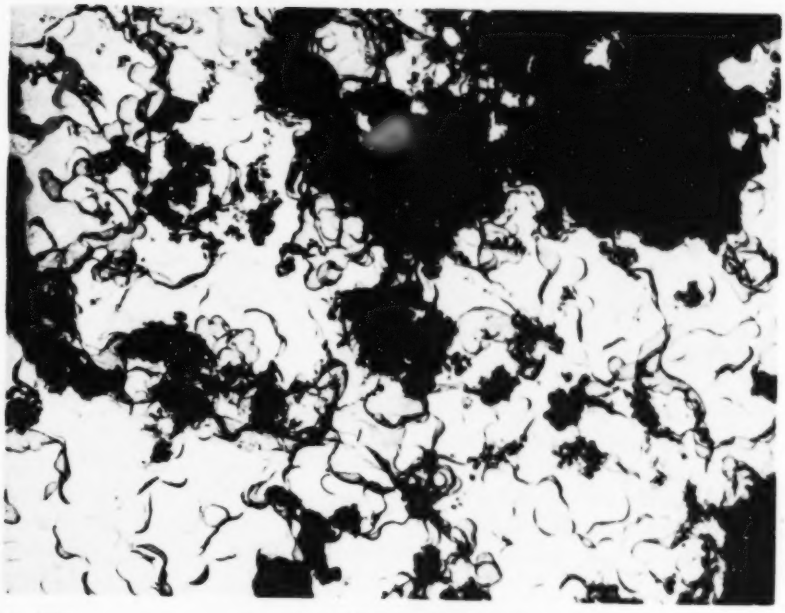
Very few insect or plant fragments were found in any of the samples studied. This is probably because the samples were collected during the winter.

Electron and light micrographs are included in this report. The electron micrographs are presented in Figures 1 through 12, and the light micrographs are shown in Figures 13 through 24.



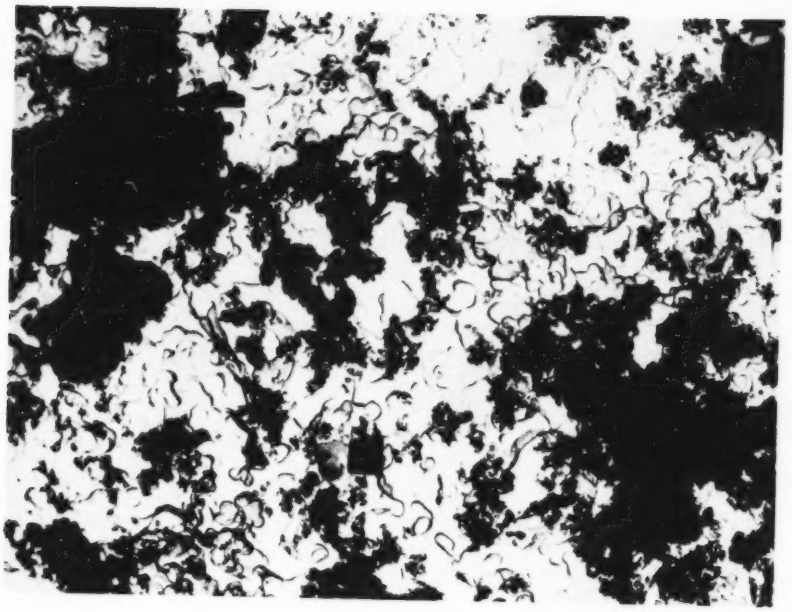
10,000X Sample M 000 405 (Cincinnati) J18801

FIGURE 1. SAMPLE CONTAINS A FRAGMENT OF A GLASS FIBER, FLYASH, AND CARBON BLACK PARTICLES



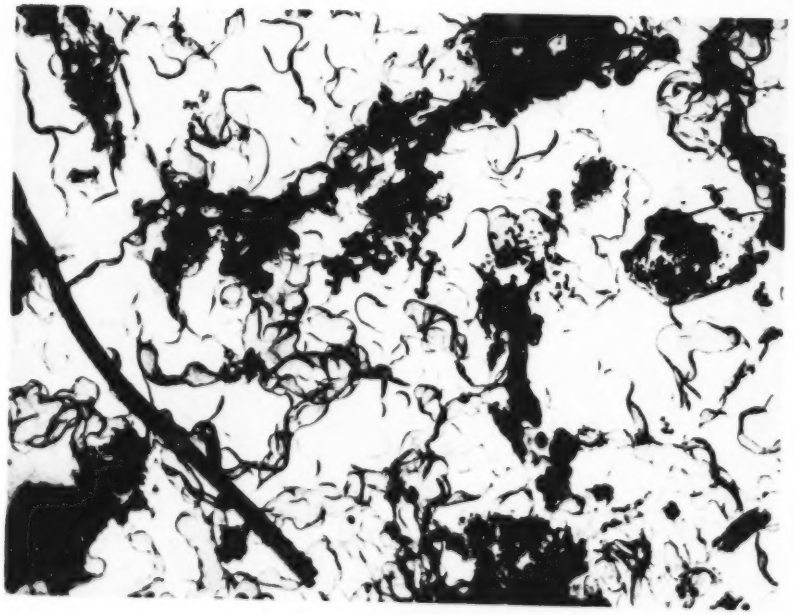
10,000X Sample M 000 406 (Washington) J18804

FIGURE 2. SAMPLE CONTAINS PRIMARILY FLYASH AND CARBON BLACK PARTICLES



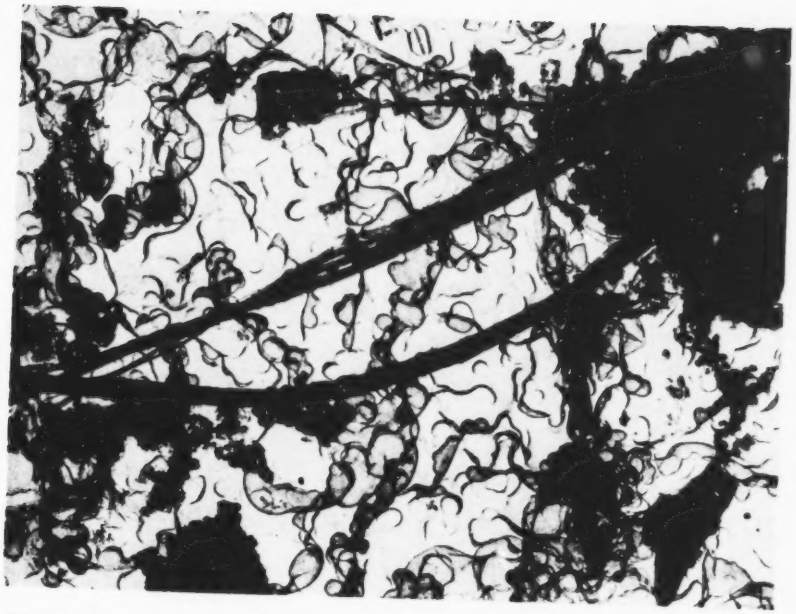
10,000X Sample M 000 407 (Washington) J18816

FIGURE 3. SAMPLE CONTAINS FLYASH, CARBON BLACK, AND A CUBIC CRYSTAL WHICH MAY BE NaCl



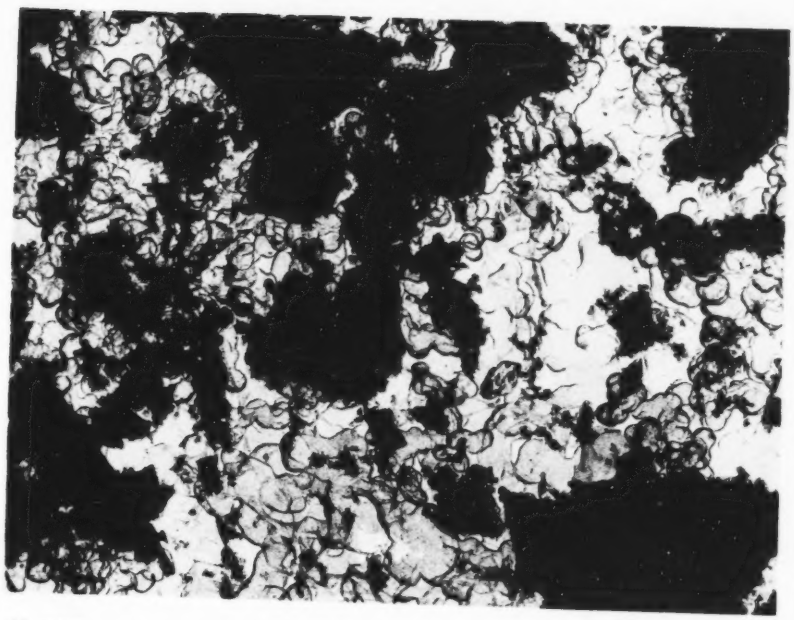
10,000X Sample M 000 408 (St. Louis) J18822

FIGURE 4. SAMPLE CONTAINS CARBON BLACK, FLYASH, AND ASBESTOS FIBERS



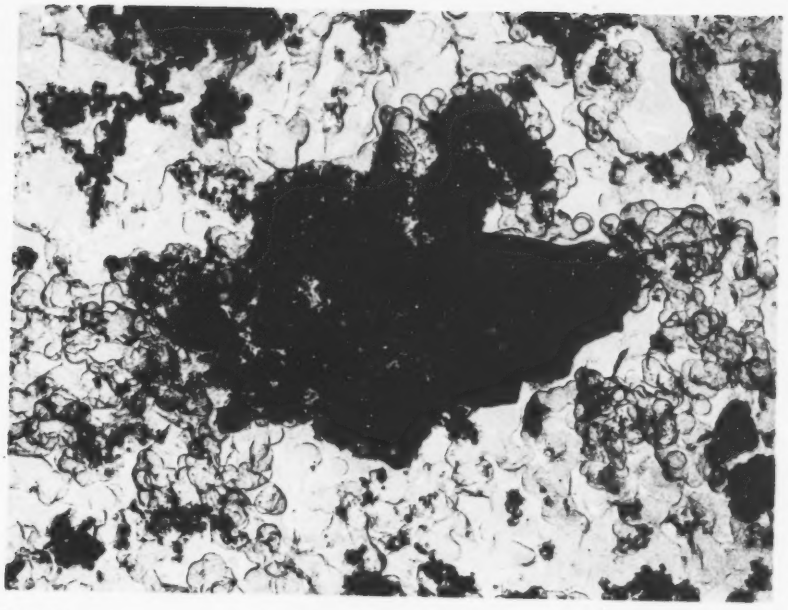
10,000X Sample M 000 409 (St. Louis) J18823

FIGURE 5. SAMPLE CONTAINS ASBESTOS FIBERS, CARBON BLACK, AND FLYASH



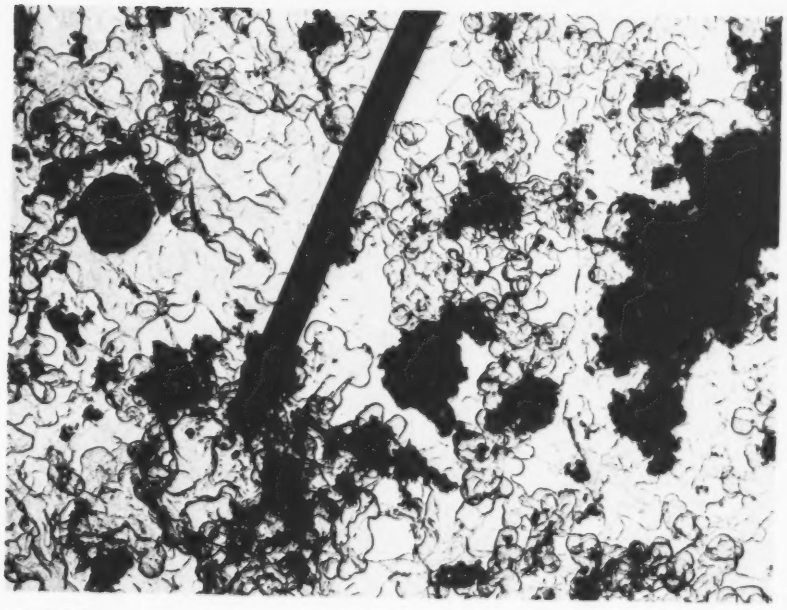
10,000X Sample M 000 412 (Denver) J18830

FIGURE 6. SAMPLE CONTAINS FLYASH, CARBON BLACK, AND FRAGMENTS WHICH ARE PROBABLY OF MINERAL ORIGIN (POSSIBLY QUARTZ)



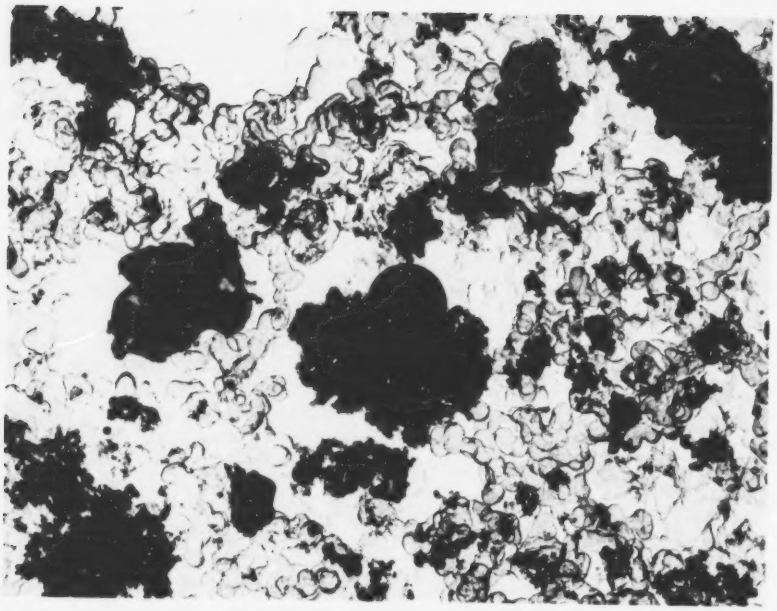
10,000X Sample M 000 413 (Denver) J18834

FIGURE 7. SAMPLE CONTAINS MINERAL FRAGMENTS, FLYASH, AND CARBON BLACK



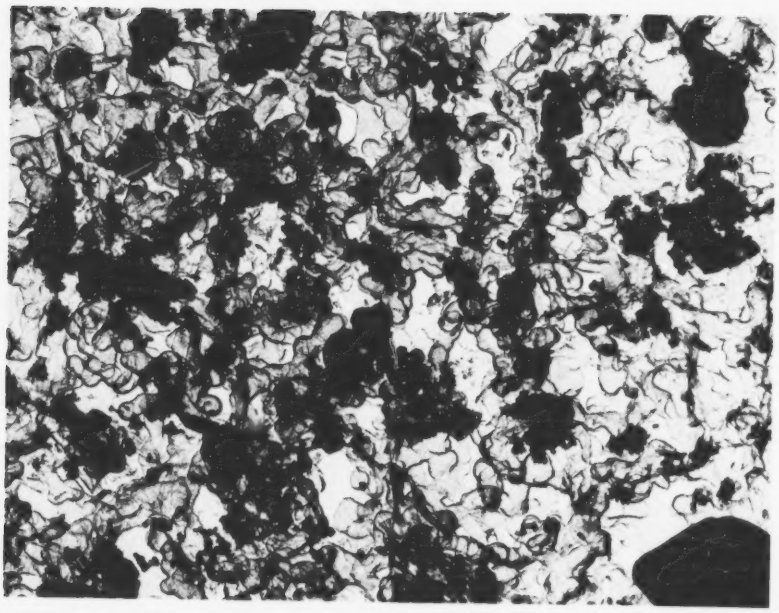
10,000X Sample M 000 416 (Cincinnati) J18839

FIGURE 8. SAMPLE CONTAINS A GLASS FIBER, CARBON BLACK, AND FLYASH



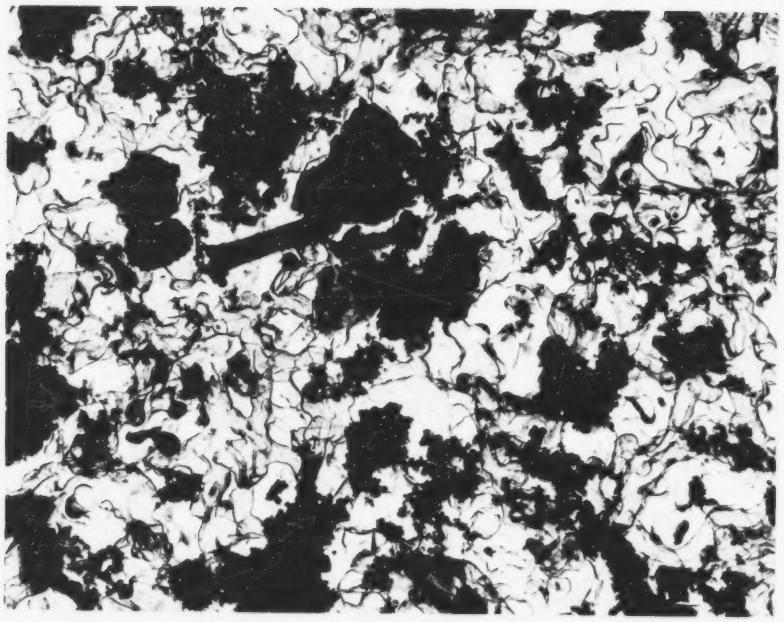
10,000X Sample M 000 417 (Cincinnati) J18847

FIGURE 9. SAMPLE CONTAINS PRIMARILY CARBON BLACK AND FLYASH



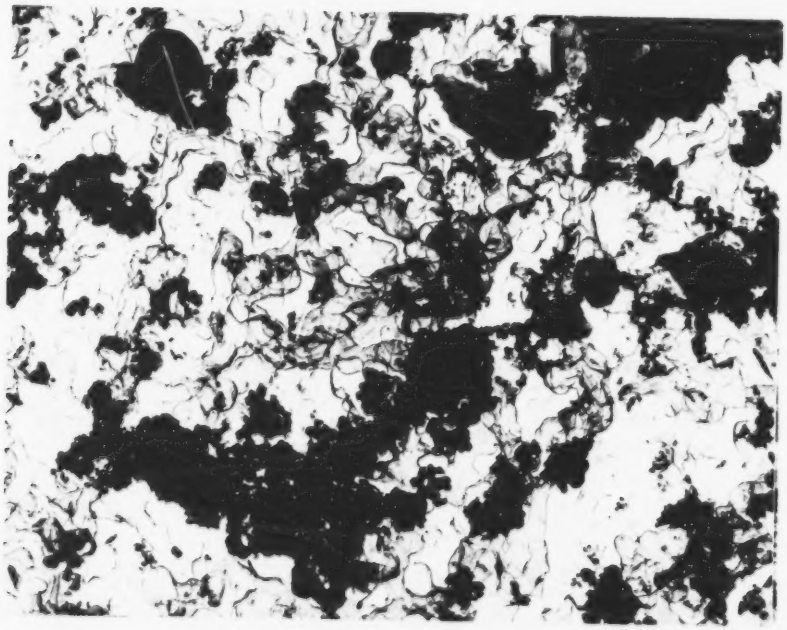
10,000X Sample M 428 (Cincinnati) J18850

FIGURE 10. SAMPLE CONTAINS PRIMARILY FLYASH AND CARBON BLACK



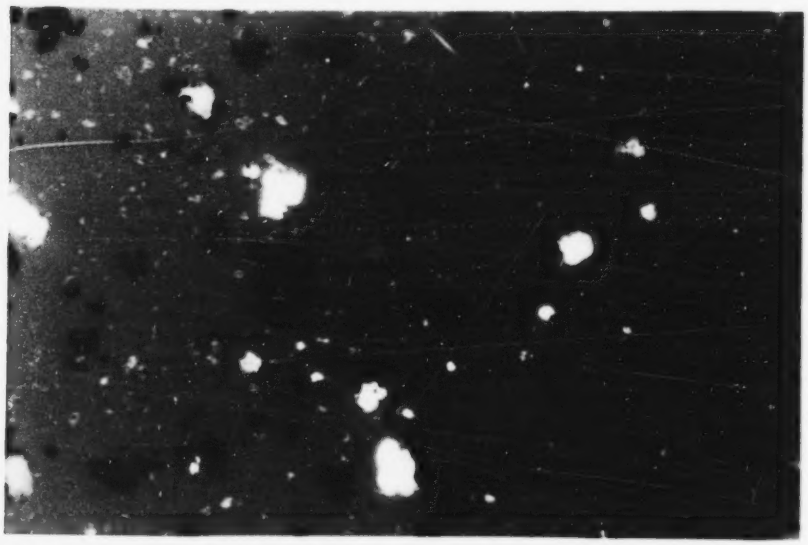
10,000X Sample M 000 419 (Chicago) J19103

FIGURE 11. SAMPLE CONTAINS PRIMARILY CARBON BLACK, FLYASH, AND MINERAL FRAGMENTS



10,000X Sample M 000 414 (Philadelphia) J19107

FIGURE 12. SAMPLE CONTAINS PRIMARILY CARBON BLACK AND FLYASH



350X 16-12 Optical Micrograph of Sample G 000 405 (Cincinnati)

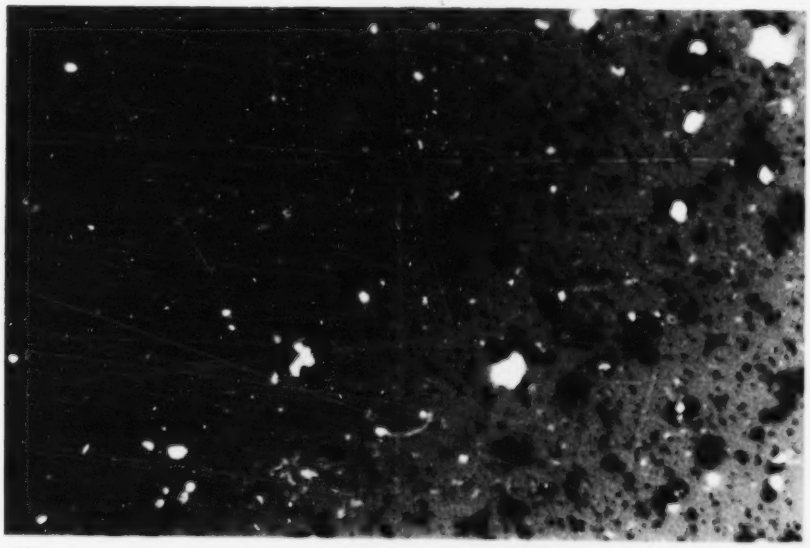
FIGURE 13. SAMPLE CONTAINS CARBON BLACK, MINERAL FRAGMENTS, FLYASH, AND IRON RUST

350X 16-15 Optical Micrograph of Sample G 000 406 (Washington)

FIGURE 14. THE MOST PREVALENT PARTICLES OBSERVED IN THIS SAMPLE ARE CARBON BLACK, MINERAL FRAGMENTS, FLYASH, AND IRON RUST

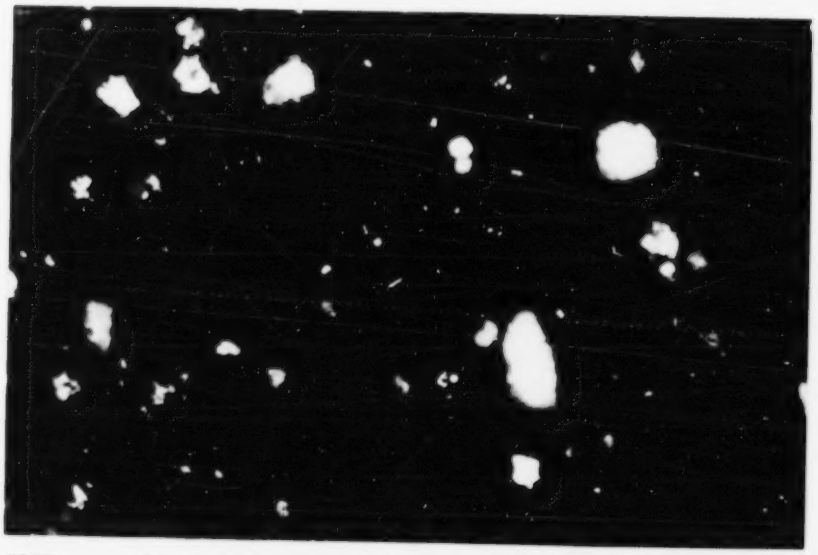
350X 17-16 Optical Micrograph of Sample G 000 407 (Washington)

FIGURE 15. THIS SAMPLE WAS FOUND TO CONTAIN CARBON BLACK, MINERAL FRAGMENTS, FLYASH, AND IRON RUST PARTICLES



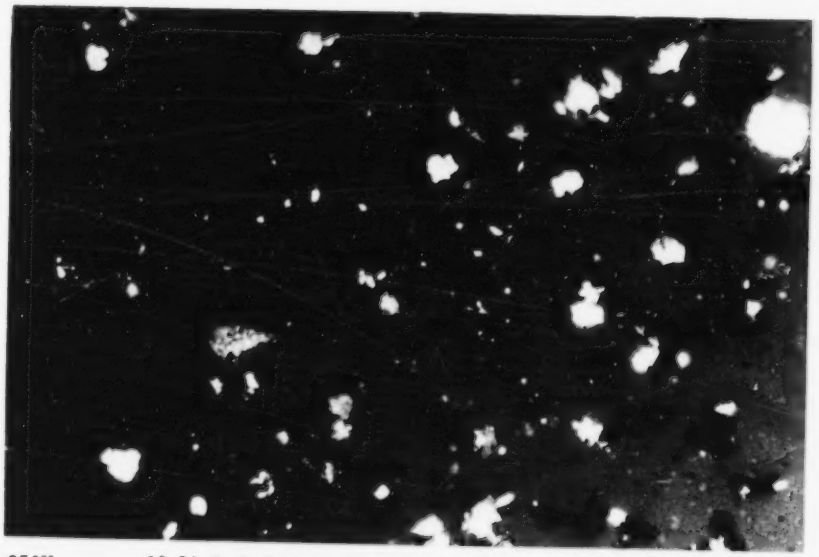
350X 16-18 Optical Micrograph of Sample M 000 408 (St. Louis)

FIGURE 16. THERE WERE FEWER LARGE PARTICLES (>10.0 μ) IN THIS SAMPLE. THE PREVALENT PARTICLE TYPES FOUND WERE CARBON BLACK, FLYASH, QUARTZ, AND IRON RUST



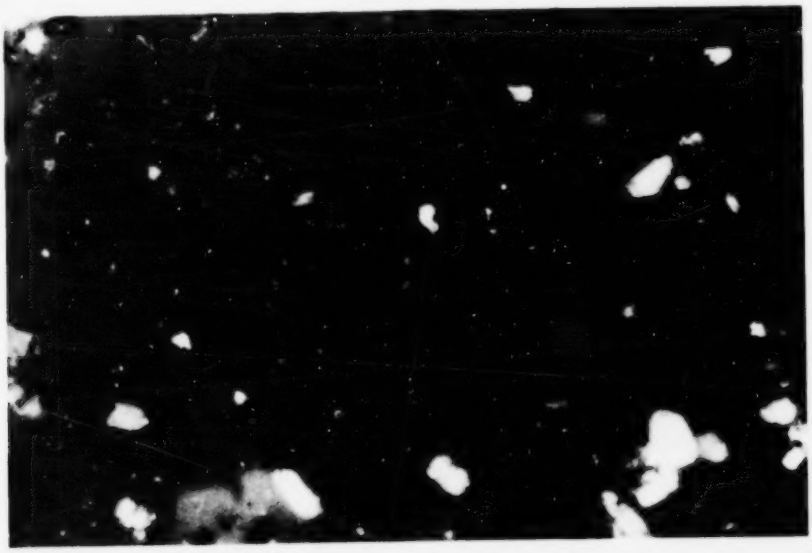
350X 16-20 Optical Micrograph of Sample M 000 409 (St. Louis)

FIGURE 17. SAMPLE CONTAINS MANY LARGE PARTICLES IN CONTRAST TO THE PREVIOUS SAMPLE ALSO FROM ST. LOUIS. THIS SAMPLE CONSISTS OF CARBON BLACK MUCH OF WHICH IS OIL SOOT; QUARTZ, AND FLYASH



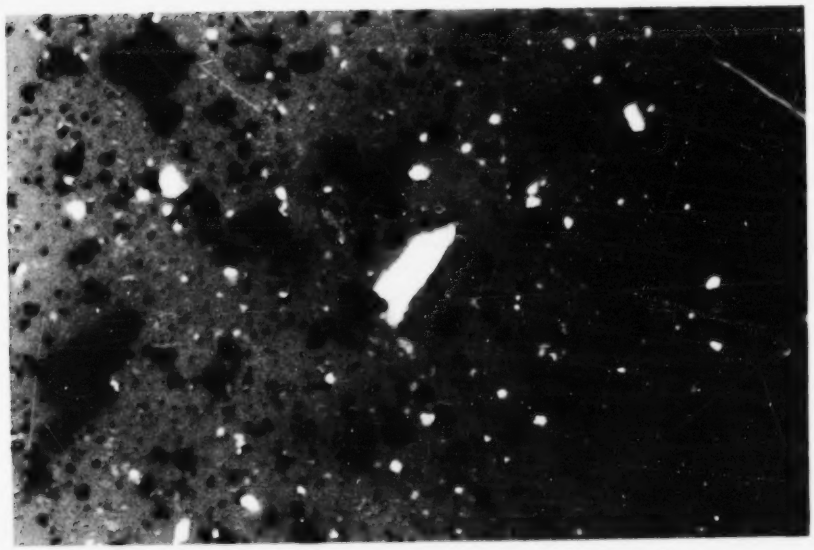
350X 16-21 Optical Micrograph of Sample G 000 412 (Denver)

FIGURE 18. THIS SAMPLE CONTAINS MOSTLY FLYASH, MINERAL FRAGMENTS, AND CARBON BLACK



350X 16-25 Optical Micrograph of Sample G 000 413 (Denver)

FIGURE 19. SAMPLE CONTAINS MANY MINERAL FRAGMENTS (MOSTLY QUARTZ) AND FLYASH. LARCE CARBON BLACK PARTICLES ARE NOT SO PREVALENT AS IN MOST OF THE SAMPLES STUDIED

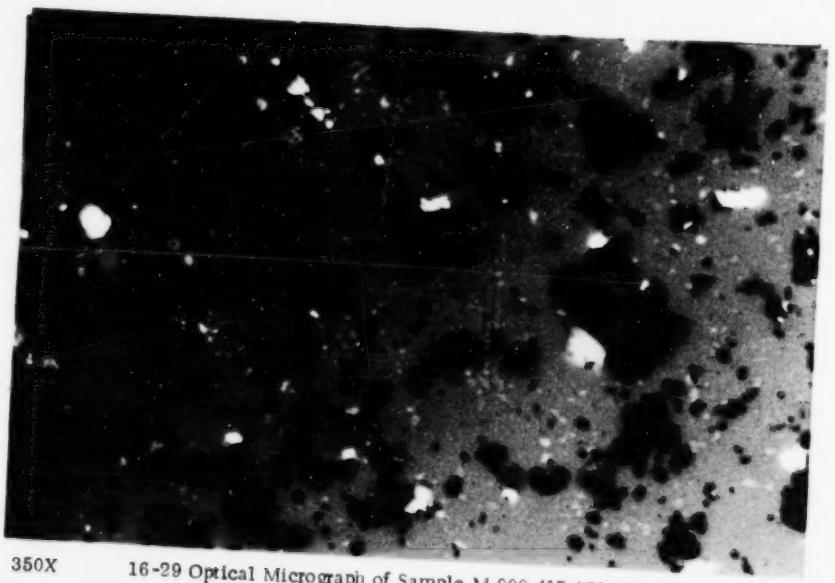


350X 17-15 Optical Micrograph of Sample G 000 414 (Philadelphia)

FIGURE 20. THE MOST PREVALENT PARTICLE TYPE IS OIL SOOT CARBON BLACK; ALSO PRESENT ARE FLYASH AND MINERAL FRAGMENTS

350X 16-26 Optical Micrograph of Sample G 000 416 (Cincinnati)

FIGURE 21. SAMPLE CONTAINS PRIMARILY CARBON BLACK AND MINERAL FRAGMENTS

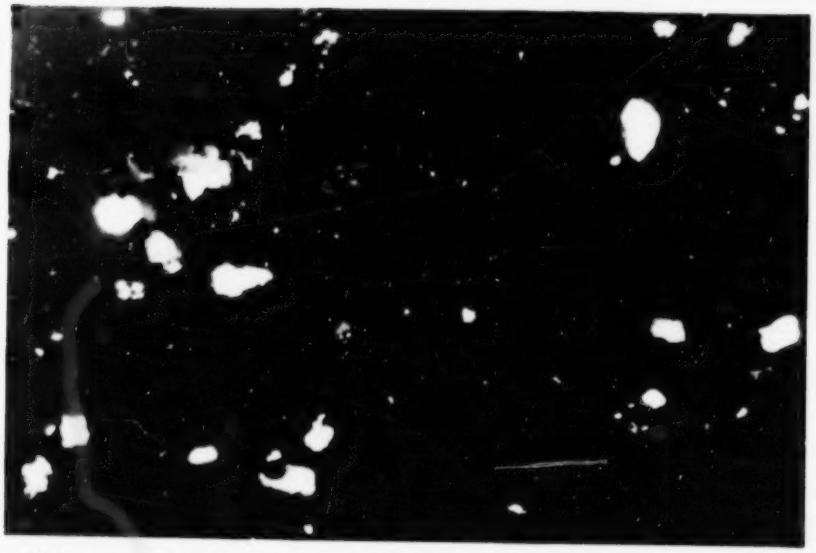


350X 16-29 Optical Micrograph of Sample M 000 417 (Cincinnati)

FIGURE 22. SAMPLE CONTAINS MOSTLY SOOT; ALSO PRESENT ARE FLYASH, MINERAL FRAGMENTS, AND IRON RUST

350X 17-16 Optical Micrograph of Sample G 000 419 (Chicago)

FIGURE 23. SAMPLE CONTAINS OIL SOOT, CARBON BLACK, MINERAL FRAGMENTS, FLYASH, AND IRON RUST



350X 16-33 Optical Micrograph of Sample 428 (Cincinnati)

FIGURE 24. SAMPLE CONTAINS CARBON BLACK, MINERAL FRAGMENTS, AND FLYASH

Future Work

During the past contract period, little emphasis was placed on the identification of the various species of airborne particulates; however, in the new contract period, particle identification will constitute a major effort. It is planned to identify particles not only through recognition of characteristic morphology observed by means of the light and electron microscopes, but also from electron-probe and X-ray and electron diffraction data. The analyses will be performed on specially prepared specimen, designed to facilitate the correlation of data from all possible sources in an effort to generate more complete information on each particulate species. This may aid in singling out the contributing sources to air pollution within a particular area.

In general there are two planned approaches to specimen preparation; one involves the analysis of single particles, and the other involves the analysis of separated particle fractions. Single-particle analyses will be made on specimen preparations suited to locating the same particle for analysis by microscopy, electron diffraction, and the electron probe. Also attempts will be made to devise and employ procedures to separate particle collections into fractions according to species and to subject portions of each fraction to various analytical techniques to yield more detailed analytical data.

Electron Microprobe

This technique logically follows elemental analysis and precedes structure identification techniques. Knowledge of which elements to seek saves probe time; the probe data on elemental associations help, for example, in XRD identification of compounds.

In the present work, the probe was used to examine Millipore filters as received. They were sufficiently conductive so as not to require coating. Figures 25 through 80 show the results obtained by examining areas of the filter for selected elements including Pb, Br, Zn, Cu, Fe, Cl, S, and P. In the Denver sample lanthanum and cerium were also sought because these elements had been found in fairly high amounts by SSMS. One area of lanthanum and cerium was located. It is observed that the lead is present not as the chloride or bromide but as the sulfate, in some cities. In St. Louis there seems to be some association of bromine with lead. Note also the areas of vanadium in the Washington sample.

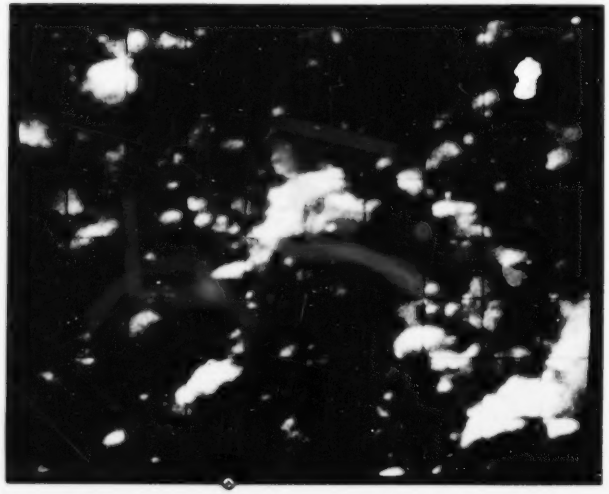
Benzene Extraction

Benzene extractions of Millipore filters were accomplished as described under Specimen Preparation in the section on Light and Electron Microscopy. The benzene-soluble phase was examined to determine what, if any, elements other than C, H, O, and N are being overlooked in the procedure of benzene extraction prior to the elemental analysis. Two techniques were employed.

First, high-resolution mass spectra were obtained of the benzene extracts from Chicago, St. Louis, Denver, and Washington. Low-resolution mass spectra were obtained of these samples and of those from Cincinnati and Philadelphia.

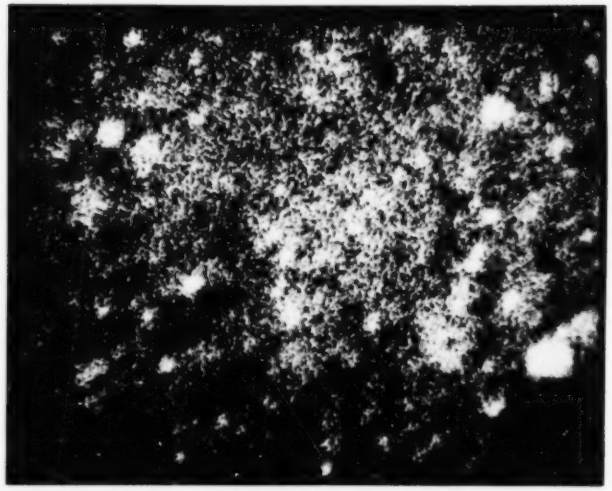
The benzene extracts were introduced into the mass spectrometer via the heated-inlet system. A sufficient amount of sample was used to produce a source pressure of 1×10^{-6} torr. None of the samples showed evidence of organometallic compounds of volatility similar to the solvent, although the methods employed do not exclude the presence of trace compounds less volatile than benzene.

A computer analysis of one of the high-resolution spectra is shown in Figure 81. The many "NO SATISFACTORY FIT" messages appearing on the leading edge of the m/e77 peak resulted from a multiplier cascade occurring, and do not represent actual species present in the spectrum.



500X

FIGURE 25. B. S. E. IMAGE, CINCINNATI SAMPLE M 000 405

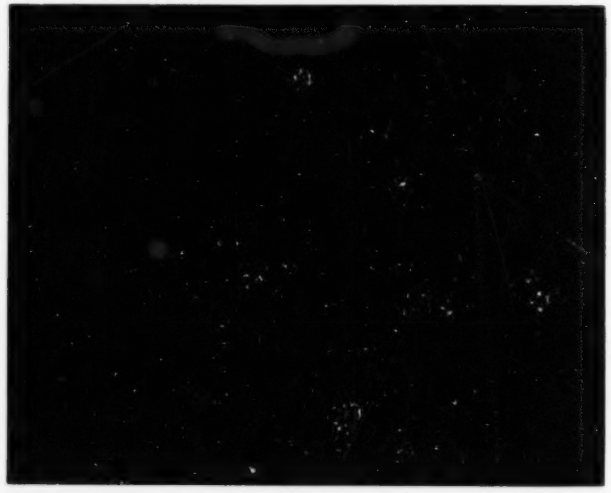


500X

FIGURE 26. Fe DISTRIBUTION IN AREA SHOWN IN FIGURE 25

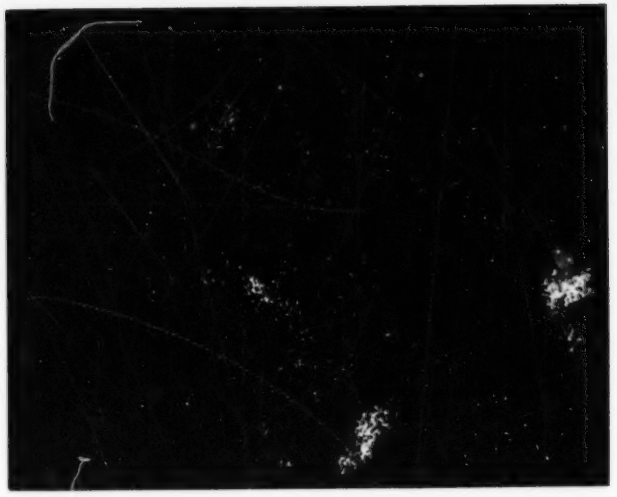
500X

FIGURE 27. Pb DISTRIBUTION IN AREA SHOWN IN FIGURE 25



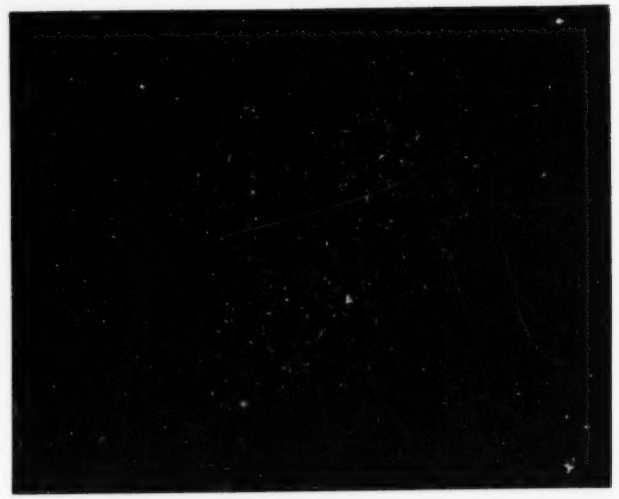
500X

FIGURE 28. S DISTRIBUTION IN AREA SHOWN IN FIGURE 25



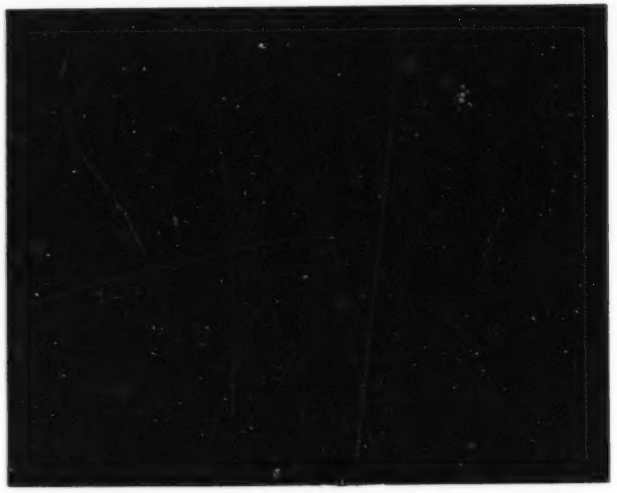
500X

FIGURE 29. Zn DISTRIBUTION IN AREA SHOWN IN FIGURE 25



500X

FIGURE 30. Cu DISTRIBUTION IN AREA SHOWN IN FIGURE 25

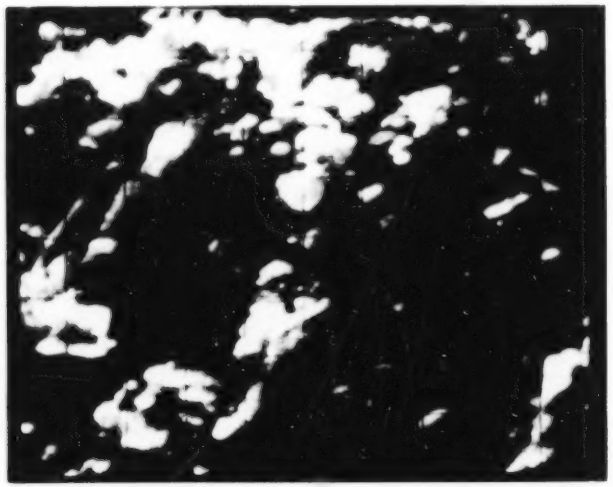


500X

FIGURE 31. P DISTRIBUTION IN AREA SHOWN IN FIGURE 25

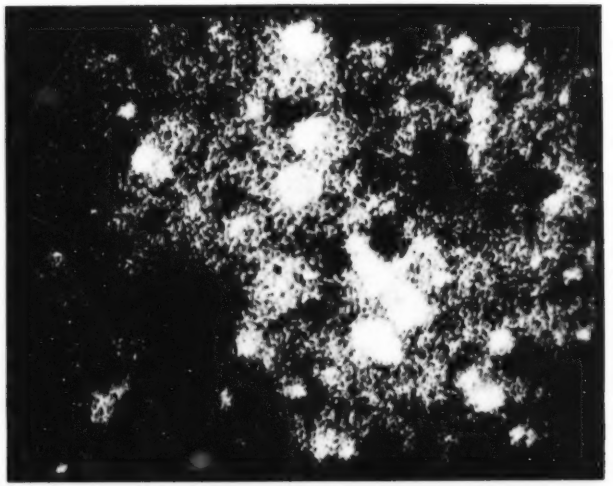
500X

FIGURE 32. Cl DISTRIBUTION IN AREA SHOWN IN FIGURE 25



500X

FIGURE 33. B. S. E. IMAGE, DENVER SAMPLE M 000 413

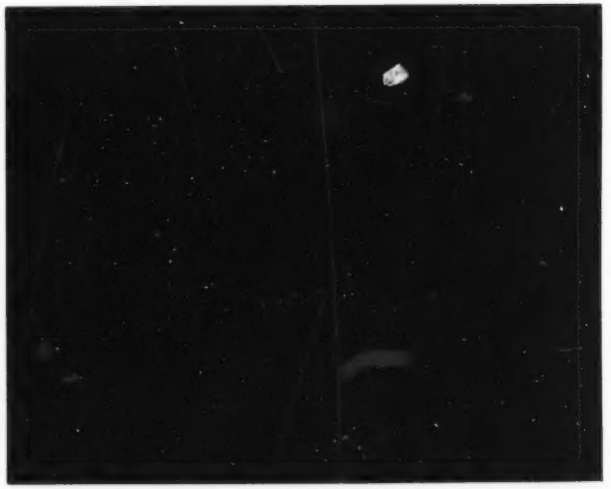


500X

FIGURE 34. Fe DISTRIBUTION IN AREA SHOWN IN FIGURE 33

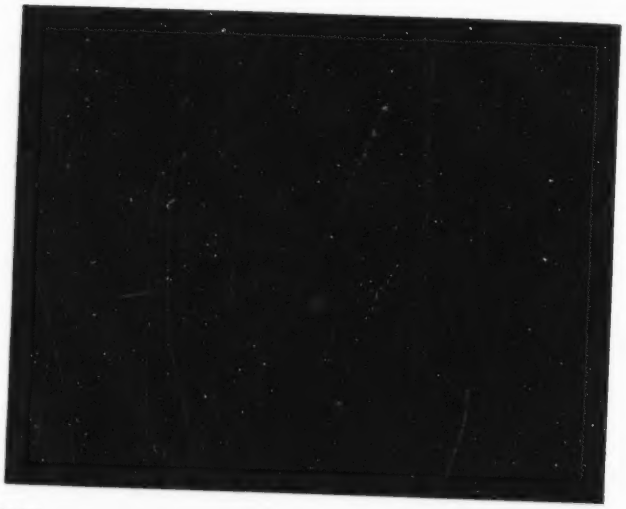
500X

FIGURE 35. Pb DISTRIBUTION IN AREA SHOWN IN FIGURE 33



500X

FIGURE 36. S DISTRIBUTION IN AREA SHOWN IN FIGURE 33



500X

FIGURE 37. Zn DISTRIBUTION IN AREA SHOWN IN FIGURE 33

500X

FIGURE 38. Cu DISTRIBUTION IN AREA SHOWN IN FIGURE 33

500X

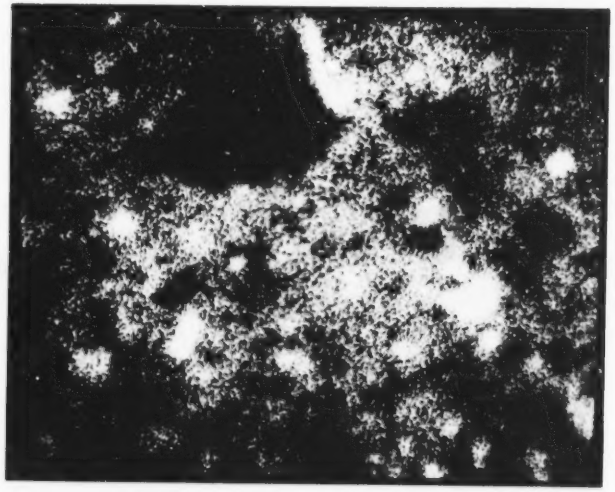
FIGURE 39. P DISTRIBUTION IN AREA SHOWN IN FIGURE 33

500X

FIGURE 40. Cl DISTRIBUTION IN AREA SHOWN IN FIGURE 33

500X

FIGURE 41. B. S. E. IMAGE DENVER SAMPLE M 000 412



500X

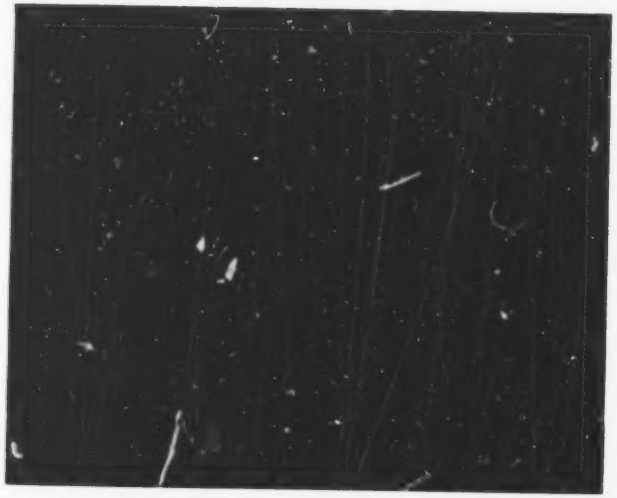
FIGURE 42. Fe DISTRIBUTION IN AREA SHOWN IN FIGURE 41

500X

FIGURE 43. Pb DISTRIBUTION IN AREA SHOWN IN FIGURE 41

500X

FIGURE 44. Cu DISTRIBUTION IN AREA SHOWN IN FIGURE 41

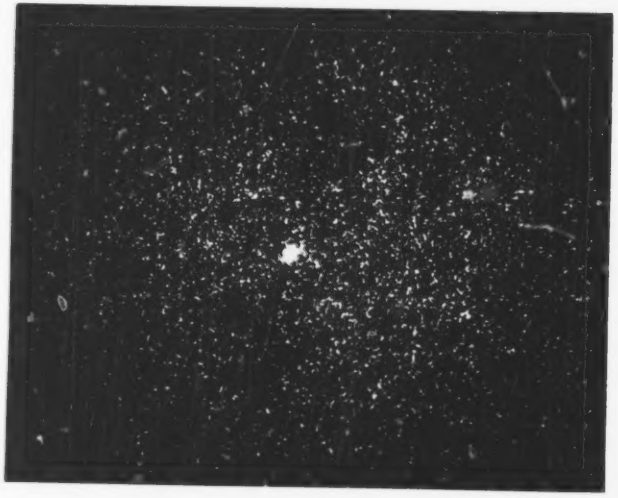


500X

FIGURE 45. P DISTRIBUTION IN AREA SHOWN IN FIGURE 41

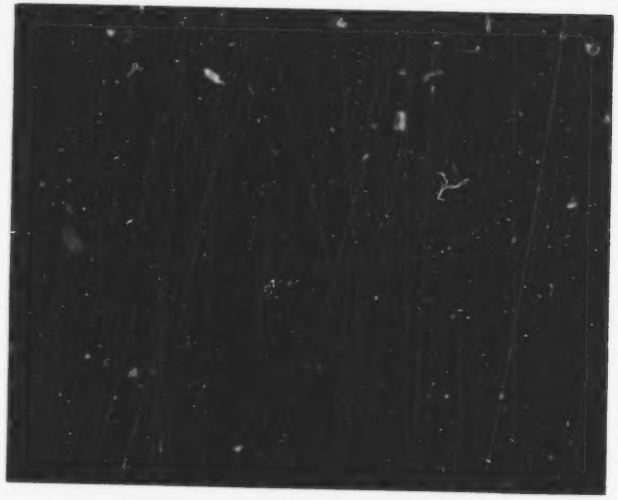
500X

FIGURE 46. Cl DISTRIBUTION IN AREA SHOWN IN FIGURE 41



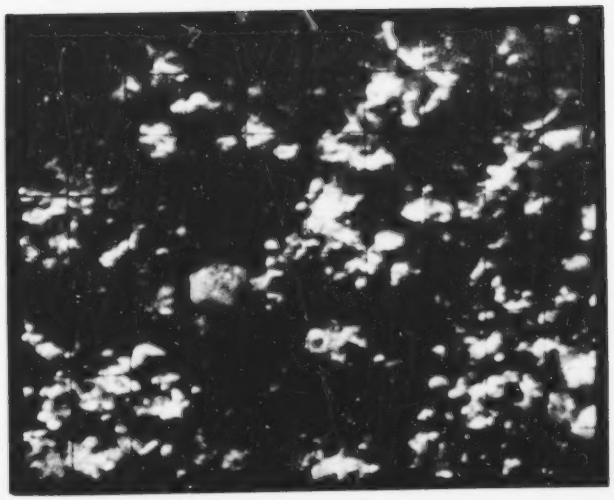
500X

FIGURE 47. La DISTRIBUTION IN AREA SHOWN IN FIGURE 41



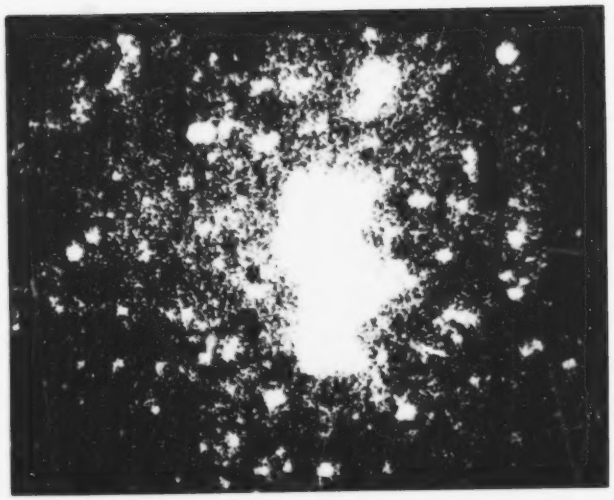
500X

FIGURE 48. Ce DISTRIBUTION IN AREA SHOWN IN FIGURE 41



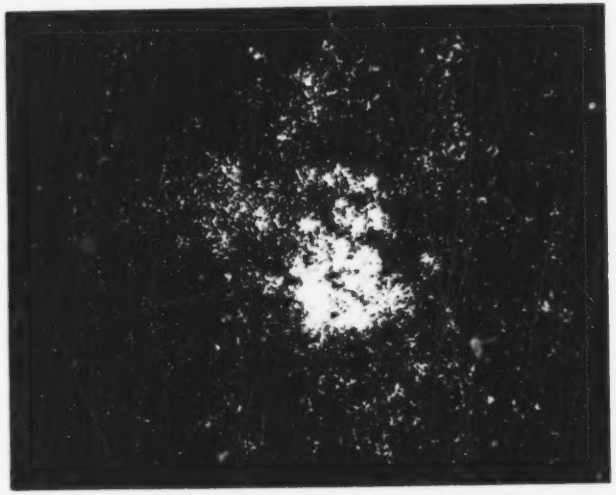
300X

FIGURE 49. B. S. E. IMAGE ST. LOUIS SAMPLE M 000 408



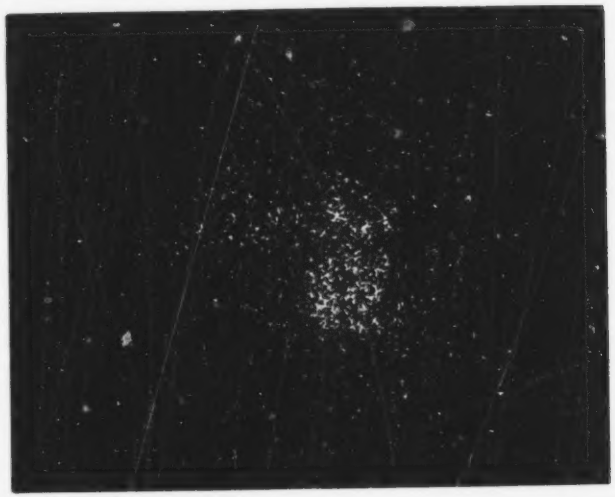
300X

FIGURE 50. Fe DISTRIBUTION IN AREA SHOWN IN FIGURE 49



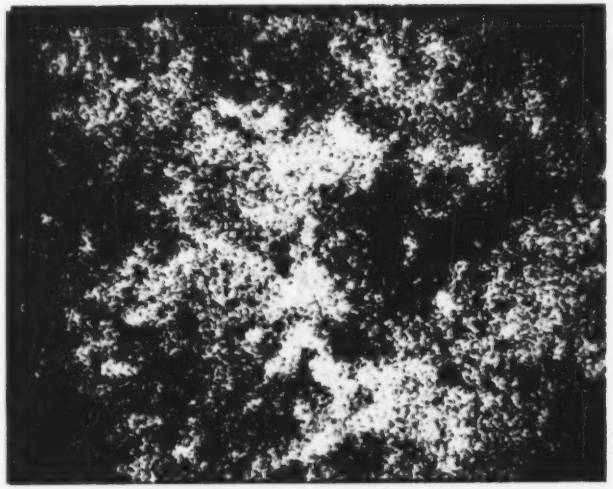
300X

FIGURE 51. Pb DISTRIBUTION IN AREA SHOWN IN FIGURE 49



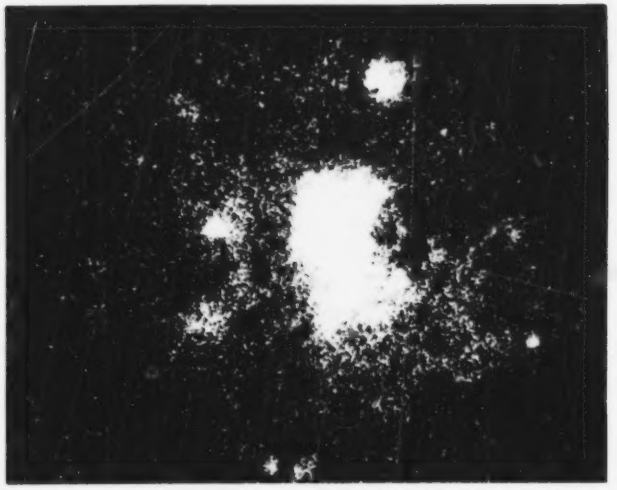
300X

FIGURE 52. Br DISTRIBUTION IN AREA SHOWN IN FIGURE 49



300X

FIGURE 53. S DISTRIBUTION IN AREA SHOWN IN FIGURE 49

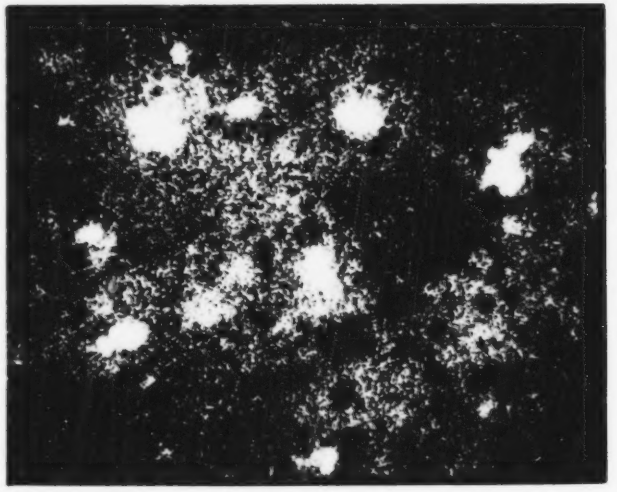


300X

FIGURE 54. Zn DISTRIBUTION IN AREA SHOWN IN FIGURE 49

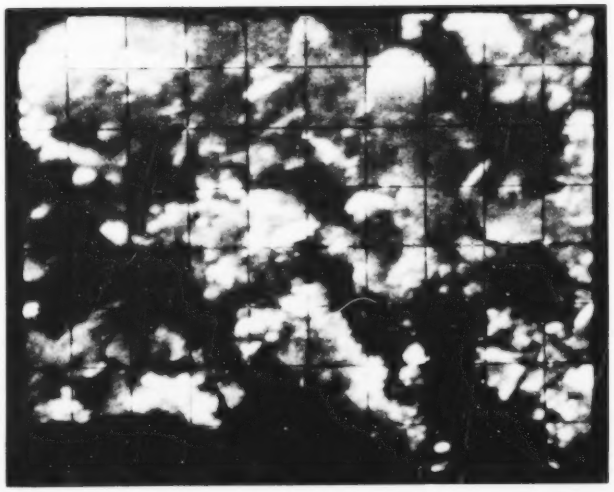
300X

FIGURE 55. P DISTRIBUTION IN AREA SHOWN IN FIGURE 49



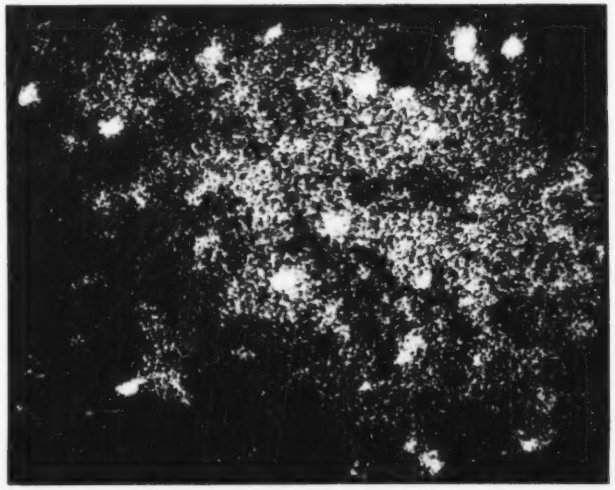
300X

FIGURE 56. Cl DISTRIBUTION IN AREA SHOWN IN FIGURE 49



500X

FIGURE 57. B.S.E. IMAGE WASHINGTON SAMPLE M 000 407

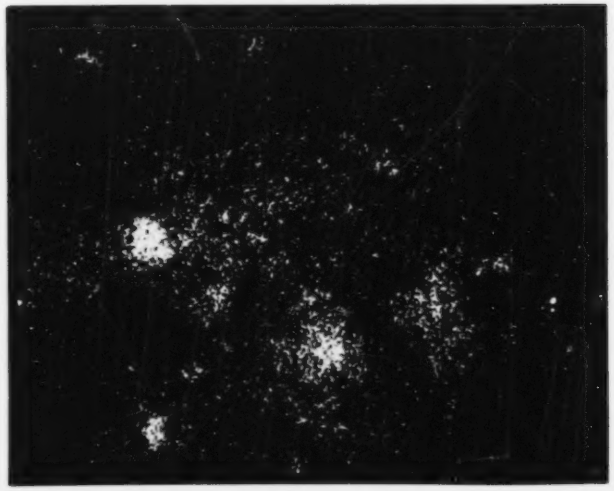


500X

FIGURE 58. Fe DISTRIBUTION IN AREA SHOWN IN FIGURE 57

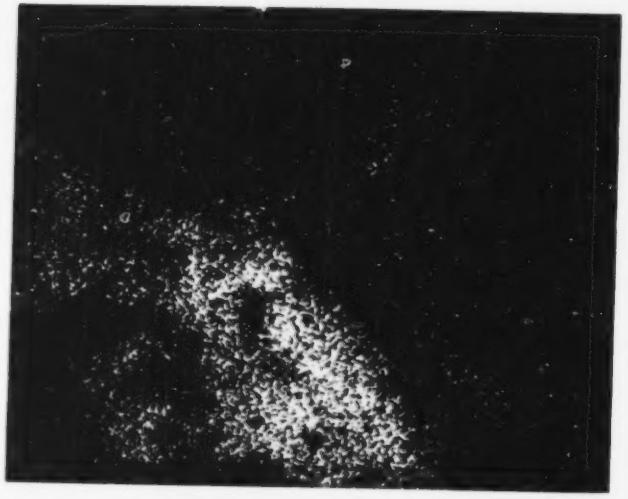
500X

FIGURE 59. Pb DISTRIBUTION IN AREA SHOWN IN FIGURE 57



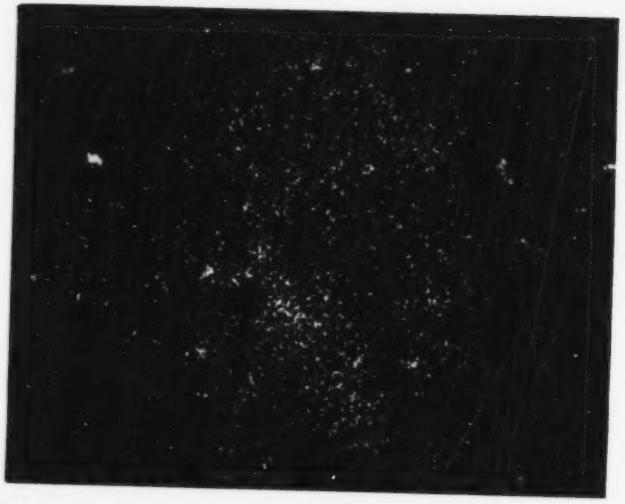
500X

FIGURE 60. S DISTRIBUTION IN AREA SHOWN IN FIGURE 57



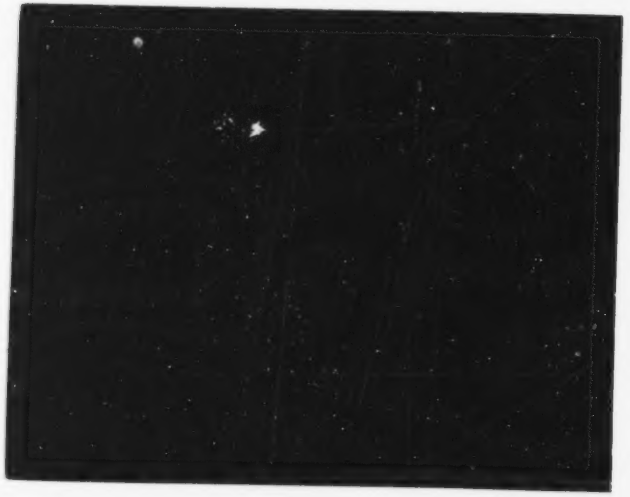
500X

FIGURE 61. Cl DISTRIBUTION IN AREA SHOWN IN FIGURE 57



500X

FIGURE 62. Cu DISTRIBUTION IN AREA SHOWN IN FIGURE 57

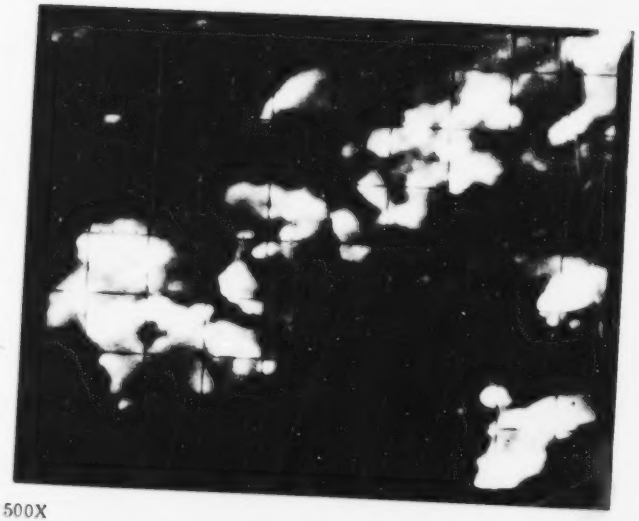


500X

FIGURE 63. V DISTRIBUTION IN AREA SHOWN IN FIGURE 57

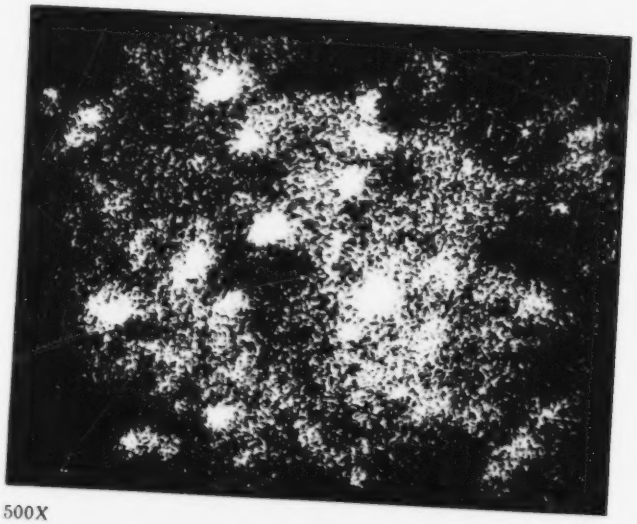
500X

FIGURE 64. Ni DISTRIBUTION IN AREA SHOWN IN FIGURE 57



500X

FIGURE 65. B. S. E. IMAGE CHICAGO SAMPLE M 000 414



500X

FIGURE 66. Fe DISTRIBUTION IN AREA SHOWN IN FIGURE 65

500X

FIGURE 67. Pb DISTRIBUTION IN AREA SHOWN IN FIGURE 65

500X

FIGURE 68. S DISTRIBUTION IN AREA SHOWN IN FIGURE 65

500X

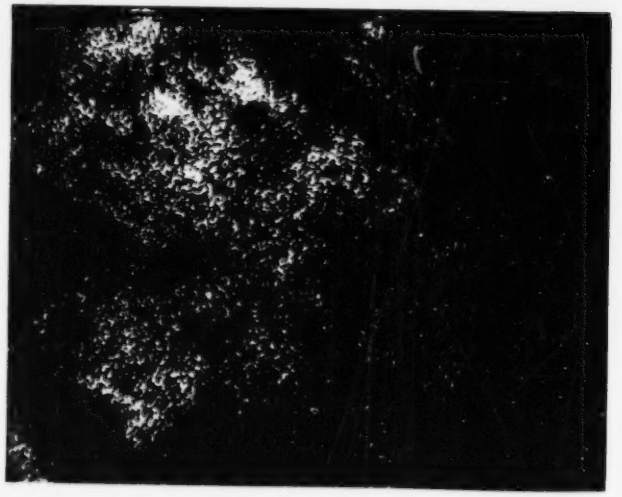
FIGURE 69. Zn DISTRIBUTION IN AREA SHOWN IN FIGURE 65

500X

FIGURE 70. Cu DISTRIBUTION IN AREA SHOWN IN FIGURE 65

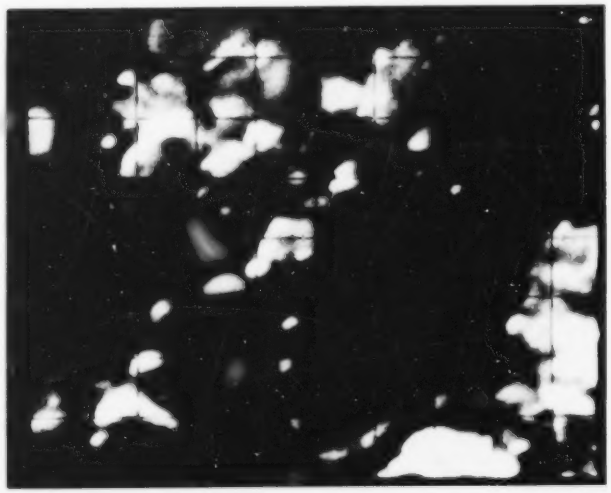
500X

FIGURE 71. P DISTRIBUTION IN AREA SHOWN IN FIGURE 65



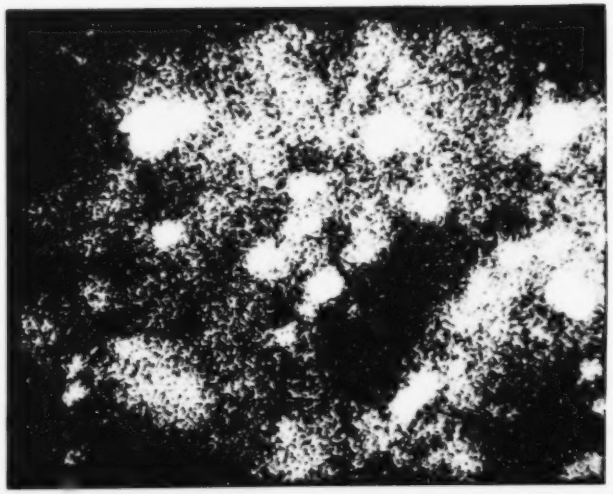
500X

FIGURE 72. Cl DISTRIBUTION IN AREA SHOWN IN FIGURE 65



500X

FIGURE 73. B. S. E. IMAGE PHILADELPHIA SAMPLE M 000 419

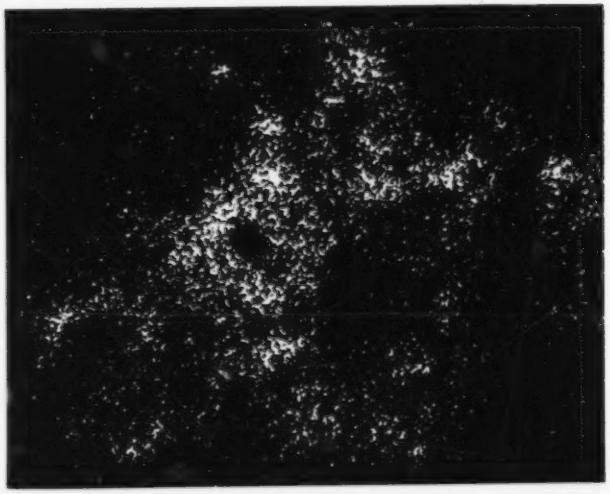


500X

FIGURE 74. Fe DISTRIBUTION IN AREA SHOWN IN FIGURE 73

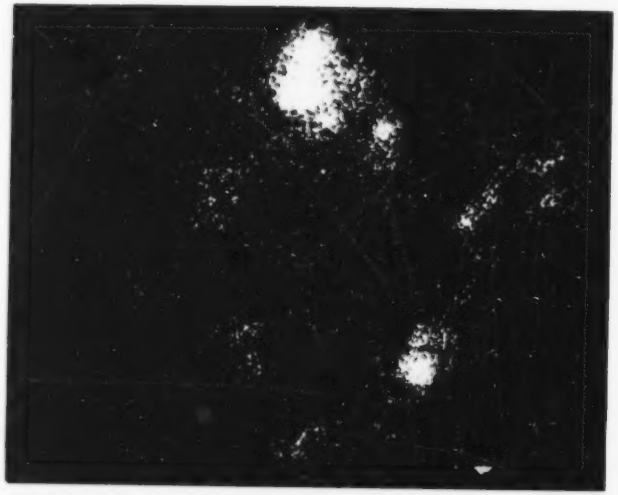
500X

FIGURE 75. Pb DISTRIBUTION IN AREA SHOWN IN FIGURE 73



500X

FIGURE 76. S DISTRIBUTION IN AREA SHOWN IN FIGURE 73



500X

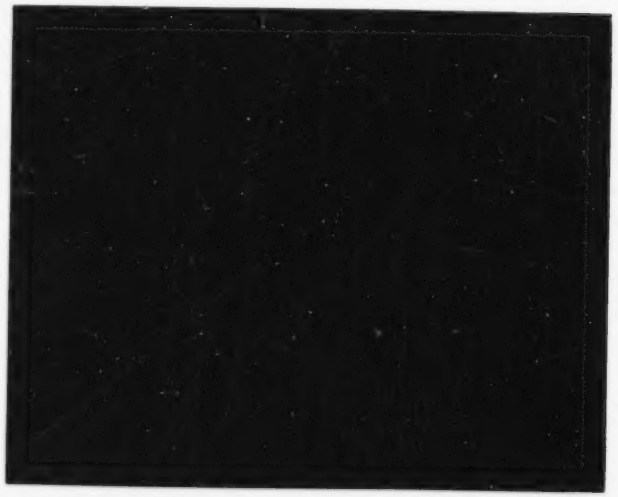
FIGURE 77. Zn DISTRIBUTION IN AREA SHOWN IN FIGURE 73

500X

FIGURE 78. Cu DISTRIBUTION IN AREA SHOWN IN FIGURE 73

500X

FIGURE 79. P DISTRIBUTION IN AREA SHOWN IN FIGURE 73



500X

FIGURE 80. V DISTRIBUTION IN AREA SHOWN IN FIGURE 73

BATTELLE MEMORIAL INSTITUTE
MASS SPECTROMETRY LABORATORY
VERSION 3 04/08/70 COMPUTER RUN DATE 06/12/70 COMPUTER JOB ID MS90274

SAMPLE MA00414 CHICAGO, WALTER

06/12/70, RUN NO. 3
SOURCE TEMPERATURE= 200 C. MULTIPLIER SETTING=0.0 AVERAGE MONITOR CURRENT=. 50. MAXIMUM MONITOR CURRENT=. 60
SAMPLE INTRODUCED VIA HEATED INLET, TEMPERATURE 200 C.
IONIZING VOLTAGE= 70 V. ACCELERATING VOLTAGE= 8 KV.
NOMINAL RESOLVING POWER 10 K
BACKGROUND HAS NOT BEEN SUBTRACTED FROM THIS SPECTRUM

CALCULATION LIMITS

ERROR (PPM)	N	O	F	CL	S4	I	S	P	SI	O	C(13)	MAXIMUM MASS
15.0	2	2	0	0	0	0	0	0	0	0	0	640

MEASURED MASS	REL. INTENSITY ACTUAL	THEOR. C(13)	CALCULATED MASS	ERROR (PPM)	FORMULA	
13.0023	.04					NO SATISFACTORY FIT
15.0200	.11					NO SATISFACTORY FIT
16.0092	.06		16.0106	77.7	N2 O	
18.0106	.94		16.0106	.0	N2 O	
25.0096	.04		25.0078	69.3	C2 H	
26.0167	1.50	.03	26.0156	42.3	C2 H2	
27.0247	1.25	.03	27.0235	44.2	C2 H3	
27.9955	.13		27.9949	19.3	C O	
28.0320	.69		28.0313	25.4	C2 H4	
36.0007	.23		36.0000	20.0	C3	
37.0093	1.99	.07	37.0078	38.9	C3 H	
37.5129	.04		75.0233		(DOUBLY IONIZED)	
38.0170	3.50	.12	38.0156	34.6	C3 H2	
38.5194	.35		77.0391		(DOUBLY IONIZED)	
39.0138	.05		78.0265		(DOUBLY IONIZED)	
39.0244	11.47	.40	39.0235	24.1	C3 H3	
39.5246	.23		79.0512		(DOUBLY IONIZED)	
40.0283	.23		80.0562		(DOUBLY IONIZED)	
40.0320	.11		40.0313	17.6	C3 H4	
42.0471	.06		42.0469	4.5	C3 H6	
44.9931	.04					NO SATISFACTORY FIT
48.0005	.20		48.0000	10.4	C4	
49.0080	1.71	.06	49.0078	3.3	C4 H	
50.0059	.14					NO SATISFACTORY FIT
50.0157	11.92	.42	50.0156	.4	C4 H2	
51.0041	.06					NO SATISFACTORY FIT
51.0233	14.70	.65	51.0235	2.5	C4 H3	
51.0377	.06					NO SATISFACTORY FIT
52.0194	.06		52.0187	13.6	C3 H2 N	
52.0316	10.36	.41	52.0313	6.2	C4 H4	
53.0367	.99	.10	53.0347	1.6	C3 C(13) H4	
55.0552	.69		55.0548	7.3	C4 H7	
59.9984	.05		60.0000	26.7	C5	
61.0044	.35		61.0078	23.8	C5 H	
62.0161	.42		62.0156	7.9	C5 H2	
63.0233	2.25	.12	63.0235	2.8	C5 H3	
64.0251	.15		64.0268	27.4	C4 C(13) H3	
			64.0273	34.4	N4 N2 O2	
68.0017	.05		68.0626	13.9	C5 H8	
68.9581	.04					NO SATISFACTORY FIT
68.9765	.23					NO SATISFACTORY FIT
72.0086	.21		72.0000	8.2	C6	
73.0082	1.53	.10	73.0078	5.6	C6 H	
74.0149	4.32	.29	74.0156	3.6	C6 H2	
75.0233	1.75	.12	75.0235	2.5	C6 H3	
76.0082	.13		76.0061	27.1	C4 N2	
76.0145	.04					NO SATISFACTORY FIT
76.0187	.09		76.0187	.6	C5 H2 N	
76.0314	6.43	.29	76.0313	3.5	C6 H4	
76.0468	.34					NO SATISFACTORY FIT
76.0620	.09		76.0627	9.5	C2 H8 N2 O	
76.0944	.10					NO SATISFACTORY FIT
78.1265	.06					NO SATISFACTORY FIT
78.1504	.07					NO SATISFACTORY FIT
78.1673	.06					NO SATISFACTORY FIT
78.1749	.08					NO SATISFACTORY FIT
78.1896	.04					NO SATISFACTORY FIT
78.3398	.05					NO SATISFACTORY FIT
78.4557	.05					NO SATISFACTORY FIT
78.5185	.04					NO SATISFACTORY FIT
78.6683	.05					NO SATISFACTORY FIT
78.7064	.09					NO SATISFACTORY FIT
78.9682	.04					NO SATISFACTORY FIT
77.0084	.05					NO SATISFACTORY FIT
77.0230	.20					NO SATISFACTORY FIT
77.0391	18.84	1.25	77.0391	7.4	C6 H5	
77.0602	.22					NO SATISFACTORY FIT
77.0691	.05		77.0715	30.4	C2 H9 N2 O	
77.7037	.78					NO SATISFACTORY FIT
78.0086	.07		78.0106	24.6	C5 H2 O	
78.0130	.12		78.0106	31.6	C5 H2 O	
78.0179	.09					NO SATISFACTORY FIT
78.0265	.48					NO SATISFACTORY FIT
78.0467	100.00	6.60	78.0469	2.7	C6 H6	
78.0902	.04					NO SATISFACTORY FIT
78.1161	.10					NO SATISFACTORY FIT
79.0311	.06		79.0296	19.2	C4 H3 N2	
79.0512	7.84	.69	79.0508	5.6	C H7 N2 O2	
		.86	79.0503	11.3	C5 C(13) H6	
80.0542	.17		80.0541	1.3	C(13) H7 N2 O2	
91.0576	.09					NO SATISFACTORY FIT
119.9928	.10					NO SATISFACTORY FIT
127.0343	.10					NO SATISFACTORY FIT
128.0620	.06		128.0626	5.0	C10 H8	
131.0294	.05					NO SATISFACTORY FIT
131.0896	.05					NO SATISFACTORY FIT
142.9945	.23					NO SATISFACTORY FIT
181.0167	.04		181.0164	1.8	C11 H3 N O2	
194.9972	.04					NO SATISFACTORY FIT
214.9992	.04		215.0007	7.1	C14 H N O2	
218.9266	.05					NO SATISFACTORY FIT

(Multiplier cascade occurred - not actual ionic species)

* Reference Peaks

* Reference peaks

FIGURE 81.

Second, the extract was slowly evaporated at room temperature on graphite. The mixture was briquetted and sparked as a normal sample. The data obtained are shown in Table A-15.

With the exception of bromine and iodine, it is clear that the amounts of the elements found in the extracted fraction are quite small compared with the total amounts in the samples. The presence of bromine and iodine, on the other hand, suggests that these elements should be sought in the benzene phase when a complete analysis is desired. If this work is repeated under the new contract, the benzene extract should be concentrated by careful drying and analyzed again, using the high-resolution mass spectrometer. The computer program should be set to accept bromine and iodine in its computations – this can be done very easily.

The amounts of benzene-soluble material on the glass filters are shown in Table A-16. If one compares these data with those in Table A-14 (C, H, and N in as-received and in extracted samples), the amount extracted (Table A-16) agrees quite well with the difference in carbon and hydrogen values in Table A-14. (Unfortunately, owing to poor coordination, different filters were run for Denver, Chicago, and St. Louis.)

X-Ray Diffraction

Although this effort is a part of the new contract, some preliminary XRD work was performed under the present contract. The major emphasis was on the Denver air sample (M 000 412). Considerable hand searching of the XRD files was done in order to positively identify the major compounds present. In addition, computer searches of the data have produced tables of possible compounds which could now be manually compared in order to provide positive identifications. An example of the computer search is shown in Figure 82.

The hand searching of the data files for the Denver air sample has identified the major X-ray diffractor to be SiO_2 (α-quartz). A probable minor constituent is muscovite mica. The probable compounds that have been selected by the computer search constitute many categories of similar structures. Among these, the sulfates, silicates, alumino-silicates, carbonates, borates, and phosphates of the metals found at 500 nanograms per cubic meter or higher predominate. No attempt was made to search for each compound manually in order to prove its existence in the sample, since it appears that a general indication of the types of structures present would be most useful at this time.

Only a partial manual search was performed on the Washington, D.C., sample (M 000 406). Again, as in the Denver sample, the compound with the highest diffracting power was SiO_2 (α-quartz). Since the subtraction of the SiO_2 pattern from the diffraction data left only weak lines to work with, no other work was done on this sample.

These preliminary results show that good sample-handling techniques combined with separations of the material by several methods will give samples which can be identified and that many more compounds will be found. This work will continue throughout the coming year.

Filters Examined

The filters, with the sample weights, air volumes, and sampling dates are listed in Table A-17. When the volume was not known it was assumed to be 10,000 M^3 for glass. It is not necessary to know sample weights because the data are generated as weight of element per square centimeter and then converted by the factor total area per total volume.

TABLE A-15. ANALYSIS OF BENZENE-SOLUBLE FRACTION OF AIR PARTICULATES EXTRACTED FROM MILLIPORE FILTERS - SSMS DATA

(Nanograms/M^3)

Element	Sample Designation					
	Cincinnati M 000 428	St. Louis M 000 408	Washington M 000 407	Denver M 000 413	Philadelphia M 000 419	Chicago M 000 414
Li	0.01	0.02	0.05	--	0.02	0.004
Be	--	0.006	0.005	--	0.01	--
Na	--	20.	10.	--	6.	2.
Mg	--	7.	--	--	--	--
Al	5.	10.	7.	--	10.	0.2
Si	7.	15.	1.	0.7	5.	--
P	1.	1.	3.	--	1.	0.4
S	3.	5.	3.	--	5.	1.
Cl	7.	15.	5.	--	7.	3.
K	5.	10.	5.	--	4.	3.
Ca	10.	20.	20.	--	50.	--
V	0.2	--	3.	--	2.	--
Cr	0.3	--	--	--	--	--
Mn	3.	0.7	--	--	--	--
Fe	4.	30.	30.	--	0.7	0.2
Co	0.6	--	--	--	--	--
Ni	--	--	--	--	0.7	--
Cu	3.	3.	3.	--	5.	0.2
Zn	2.	10.	--	--	3.	0.2
As	0.2	4.	0.5	--	0.5	0.2
Br	10.	15.	100.	3.	15.	10.
Rb	--	0.5	--	--	--	--
Sr	--	1.	--	--	--	--
Sn	--	2.	--	--	--	--
I	--	2.	1.	--	1.	0.2
Ba	--	30.	1.	--	--	--
Pb	2.	10.	20.	--	6.	1.

TABLE A-16. BENZENE-SOLUBLE PORTION EXTRACTED FROM GLASS FILTERS

Sample Designation	City	C_6H_6 Extract, Nanograms/M^3
G 001	Cincinnati	17,500.
G 002	Cincinnati	17,200.
G 000 6966	Cincinnati	32,700.
G 000 6977	Cincinnati	14,000.
G 000 6978	Cincinnati	14,000.
G 000 6989	Washington	13,600.
G 000 6990	Washington	17,700.
G 000 6985	St. Louis	24,600.
G 000 6986	St. Louis	13,900.
G 000 6982	Denver	19,100.
G 000 6979	Chicago	14,400.
G 000 6967	Philadelphia	15,600.

******* OUTPUT *******

SAMPLE:C=9552=1 DENVER M-000412 DATE/TIME 15 MAY 70 10:00:01

*** THE FOLLOWING PATTERNS ARE POSSIBILITIES WHICH ARE SUBSETS OF THE UNKNOWN PATTERN OF 0 AND 1

*** NO CHEMICAL INFORMATION IS USED TO LIMIT THE FOLLOWING TABLE OF RESULTS
*** THE STAR ON THE RELIABILITY FACTOR DENOTES AGREEMENT WITH CHEMICAL INFORMATION AND THE ENTIRE PATTERN WILL APPEAR IN THE REPORT

*** THE QUESTION MARK ON THE RELIABILITY FACTOR DENOTES DIFFICULTY WITH THE CHEMICAL FORMULA

NUMBER OF LINE MATCHES	PERCENT OF STANDARD LINE MATCHES	MINIMUM INTENSITY OF LINES COMPARED	LOG INT MATCH	ASTM NUMBER	DATA MARK	FORMULA	ALLOY PHASE DES.	RELIABILITY FACTOR
11	57	25	3	10383		CO (NH 03)2 . H2 O		5
11	57	10	6	10385		MG SR 03 . 6 H2 O		17
9	56	25	3	10388		NI (C N)2 . 4 H2 O		10
13	54	25	3	10392		SR2 (S 04)3		11
8	66	3	25	10397	*	NA AL (S 04)2 . 12 H2 O		15
14	66	25	3	10411		LI I . 3 H2 O		6
14	66	10	6	10417		ZN H P 03 . 2= 1 / 2 H2 O		7
12	90	15	6	10419		LI2 CR 04		15
12	63	15	6	10429		MG I2 . 8 H2 O		10
14	51	15	6	10432		CA BI P6		3
7	50	25	3	10482		K ZN (C N)3		8
9	64	10	10	10491		CU C N		22
7	87	3	10	10492		RA YI F6		19
8	57	10	10	10908		K2 CA FE (C N)6		12
6	66	25	3	10915		AL I3		12
8	61	25	3	10970		BARIUM PHOSPHITE		117
10	50	25	3	10977		ZN (P 03)2		26
11	73	10	10	10987		NA2 S2 O8		15
9	50	10	6	10994		FE S 04		22
9	56	15	6	10703		CA CL2 . CA (H2 P 04)2 . 2 H2 O		15
9	64	25	3	10704		ZN H AS 04 . H2 O		14
11	73	25	3	10711		TE CL2		17
21	52	15	6	10712		K2 SI 07		12
14	61	25	3	10717		3 (BR, K2) CR 04 . 2 H2 O		19
9	50	10	10	10719		SB AS 04		13
14	69	15	6	10728	*	K I 03		25
6	66	6	10	10776		ZINC ARSENITE		157
10	71	25	3	10777		BA3 (O H)2 (P 04)2		3
12	57	25	3	10811		CALCIUM ARSENITE		147
9	50	25	3	10828		CA (S C N)2 . 3 H2 O		15
12	66	6	10	10829		SB SN		24
9	71	15	6	10830		HG2 S 04		4
12	59	25	3	10838		N H4 MN P 04 . H2 O		19
11	52	15	6	10968		ZN SE 03 . H2 O		21
10	71	6	15	10979		MN3 (P 04)2 . 7 H2 O		4
6	59	25	3	11098	*	CU C02 04		22
8	59	25	3	11155		CS2 AU (AU CL6)		9
8	53	25	3	20321		NA= CA= AL= SI= O= S O		15
8	72	25	3	20331		PB3 AS2 S8		13
20	51	25	3	20538		MN3 (P 04)2 . 6 H2 O		9
9	52	25	3	30020		MG N H4 P 04 . H2 O		15
7	69	25	3	30028		N H4 CR (S 04)2		13
10	62	25	3	30032		(N H4)3 FE (P 04)3		23
9	69	6	10	30043		(N H4)3 AL (S 04)3		18
10	58	10	10	30045		LA2 (S 04)3		8
12	57	25	3	30074		LI4 P2 07		7
12	59	15	6	30222		CU (N H3)4 S 04		21
6	59	15	6	30273		H3 P 03		4
7	50	25	3	30297		NA4 AL3 CL B13 O12		20
6	54	25	3	30338		FE P 04		6
14	55	15	6	30379		K3 FE (S 04)3		11
8	53	15	6	30450		K B 02		22
9	79	15	6	30729		CA2 SI		11*
5	71	25	3	30798		FE2 B		28
8	79	6	10	31093		SR (N 03)2		19
9	52	15	6	40310	*	TI O2		4
6	50	25	3	40477	*	TE		15
9	52	15	6	40554	*	K CL		19
9	71	15	6	40587	*	U3 SI2		8
10	62	25	3	40730		2 NA2 C 03 . 3 H2 O2		15
15	65	15	6	40749		PT		11
5	83	10	10	40802	*	BA C 03		17
13	65	15	6	50378	*	S O2		29
11	78	3	25	50428		SI O2		85
34	100	0	100	50490	*	CS I CL2		4
11	54	25	3	50537	*	NA CL		45
8	85	3	15	50628	*	MG3 AL4 Y13 O29		5
7	50	25	3	50636		CO O		8
5	62	25	3	50640	*	IN		9
9	69	15	6	50642	*	ZR		16
10	63	15	6	50645	*	CU2 O		27
6	85	25	3	50667	*	CU		17
6	54	25	3	50674	*	YI		15
8	55	15	6	50682	*	CA O . SI O2 .Y H2 O		11
7	53	25	3	60010		CA S 04 . 2 H2 O		22
15	62	15	6	60046	*	SM (O H)3		9
8	61	15	6	60117	*	GA O2 H		6
14	60	25	3	60180	*	TL P F6		15
10	62	25	3	60191	*	ZN (CL O4)2 . 6 H2 O		21
13	51	10	6	60197	*	TL I		22
15	59	25	3	60279	*	PB4 O3 S 04 . H2 O		14
12	54	15	6	60282	*	PB F2		22
20	62	15	6	60288	*	AG N O2		10
11	50	15	6	60349	*	PB SE		14
8	61	25	3	60384	*	(BA C)	SR	15
14	60	25	3	60555		(TI AS)	4T	2
6	59	25	3	60940		(CO2 W4 C)	113F	19
8	61	15	6	60611		(CO3 W3 C)	113F	15
9	62	25	3	60639		(NI2 MN SN)	18F	9
7	53	25	3	60692		(CO2 MN SN)	18F	9
8	66	25	3	60695		(MO N2)	3M	13
6	54	15	6	60982		MO .5 W 03		11
8	61	25	3	60987		CS2 SI F6		16
9	52	15	6	70006	*	K ALZ SI3 AL O10 (O H)2		18
18	62	25	3	70025	*	AM P4		21
11	68	25	3	70031		(MN3 ZN C)	9C	9
9	66	15	6	70046		ZN2 P2 O7 . 9 H2 O		20
17	65	6	15	70087	*	CO MU O4		14
13	59	25	3	70209	*	PB I2		14
10	66	15	6	70235	*	K P F6		6
7	50	15	6	70255	*			

FIGURE 82.

TABLE A-17. FILTER SAMPLES ANALYZED

Filter Number[1]	Location	Volume, M^3	Weight, g			Sampling Dates	
			Gross	Tare	Net	Start	Finish
G-0006977	Cincinnati	12,551	3.9601	2.877	1.083	12/8	12/25/69
G-0006978	"	12,900	4.1561	2.860	1.296	1/1	1/ 8/70
G-001	"	10,035	5.5135	4.024	1.490	11/24	12/ 4/69
G-002	"	7,261	5.3930	3.900	1.493	11/24	12/ 4/69
G-0006966	"	13,036	4.5540	2.852	1.702	12/4	12/11/69
M-000417	"	9,699	3.7282	2.429	1.299	1/1	1/15/70
M-000416	"	7,645	3.2267	2.434	0.793	12/18	1/ 1/70
M-000405	"	11,239	3.6867	2.438	1.249	12/4	12/18/69
M-428	"	7,628	3.7910	2.957	0.834	11/24	12/ 4/69
G-0006981	Denver	13,122	6.1610	2.810	3.351	1/2	1/ 9/70
G-0006982	"	13,122	7.1040	2.850	4.254	1/16	1/23/70
M-000412	"	12,836	6.4050	2.450	3.955	1/2	1/16/70
M-000413	"	8,272	4.434	2.433	2.001	1/16	1/30/70
G-0006985	St. Louis	7,107	4.3225	2.769	1.554	1/13	1/19/70
G-0006986	"	12,551	4.8466	2.728	2.119	1/19	1/26/70
M-000408	"	3,178	3.2834	2.477	0.806	1/13	1/19/70
M-000409	"	6,161	3.8833	2.475	1.408	1/19	2/ 2/70
G-0006989	Washington	11,011	3.5210	2.644	0.877	12/23	12/30/69
G-0006990	"	11,267	3.9144	2.666	1.248	1/6	1/13/70
M-000407	"	8,672	3.8095	2.489	1.320	1/6	1/20/70
M-000406	"	9,584	3.4600	2.495	0.965	12/25	1/ 6/70
M-000414	Chicago	18,609	?	?	?	2/11 3/3	2/19/70 3/16/70
M-000415	"	8,321	?	?	?	3/18 4/3	3/25/70 4/13/70
G-0006979	"	27,797	?	?	?	2/11	3/ 2/70
G-906280	"	11,507	?	?	?	3/18	3/25/70
G-686900	"	?	?	?	?	?	?
M-000418	Philadelphia	11,993	?	?	?	3/19	4/ 2/70
M-000419	"	12,889	?	?	?	4/2	4/16/70
G-0006967	"	9,594	?	?	?	3/19	3/26/70
G-0006968	"	10,451	?	?	?	4/2	4/ 9/70

(1) G = Glass, M = Millipore.